

JUN 21 1943

**TRANSACTIONS OF THE
AMERICAN
• SOCIETY •
FOR METALS**



JUNE, 1943

Volume XXXI

Number 2

The TRANSACTIONS *of the* AMERICAN SOCIETY FOR METALS

*Published quarterly and Copyrighted, 1943, by the AMERICAN SOCIETY FOR METALS
7301 Euclid Avenue, Cleveland 3, Ohio*

SUBSCRIPTIONS: (members) \$2.50 per year
(non-members) \$5.00 per year, \$2.00 per copy
Foreign (non-members) \$6.50 per year, \$2.50 per copy

Entered as second class matter, November 9, 1931, at the Post Office at
Cleveland, Ohio, under the Act of March 3, 1879

RAY T. BAYLESS, *Editor*

Vol. XXXI

June, 1943

No. 2

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SOME FACTORS AFFECTING LONGITUDINAL BEND TESTS ON FINE-GRAINED, COLD-ROLLED ANNEALED CARBON STRIP STEEL

BY A. F. SPRANKLE AND M. A. HUGHES

Abstract

A study was made to determine the effect of (A) chemical composition, (B) amount of cold reduction, and (C) annealing time on the longitudinal flat bend characteristics of killed, fine-grained, plain carbon strip steels. Data were obtained and curves drawn to show hardness obtained with different amounts of cold reduction and annealing times. It was found that low (0.15 to 0.20 per cent) carbon steels gave flat bends free from visible cracks, irrespective of the manganese content or the amount of cold reduction prior to annealing. The region of grain coarsening between approximately 10 and 25 per cent cold reduction prior to annealing was clearly shown. The intermediate (0.50 to 0.60 per cent) carbon grades required a minimum of 35 per cent prior cold reduction to obtain satisfactory flat bends with minimum annealing times. Low manganese content also appeared desirable. The high (0.85 to 0.95 per cent) carbon steels could not be bent flat but exhibited differences in the degree of cracking when bent on a radius equal to two times their gage thickness. A minimum of 45 per cent cold reduction prior to annealing was necessary for obtaining satisfactory bends under these conditions. Low manganese content and long annealing times appeared helpful in improving the materials' response to the bend test.

INTRODUCTION

COLD-ROLLED annealed carbon steel strip is often required to pass numerous and varied physical test requirements depending on the proposed application. Of these tests, probably none is more severe or informative than the longitudinal flat bend test when applied to killed carbon steel that is to withstand difficult cold form-

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ing and bending operations. In applying this test, the strip is bent flat on itself longitudinally to the direction of rolling. To be considered satisfactory, the stock must be free from cracks at the sharp radius of the bend.

Numerous flat bend tests, made on several different grades of steel, indicated that there are several factors which influence the satisfactory response of a given material to this test. As an outgrowth of these preliminary observations, it was decided to investigate steels of various carbon and manganese contents in an endeavor to ascertain the magnitude of some of these controlling factors. Our preliminary observations led us to believe that the factors of primary interest were: (A) Variations in chemical composition, (B) amount of cold reduction prior to annealing, and (C) annealing time.

A review of the literature disclosed that previous published work dealing directly with the response of cold-rolled annealed carbon strip steel to longitudinal flat bend tests is non-existent. However, there are several articles that have an indirect bearing on this subject.

As early as 1927, Swinden and Bolsover (1)¹ investigated steels cold-reduced 33 and 67 per cent, and containing 0.10, 0.34, 0.54, and 0.70 per cent carbon by heating for 1 hour at 200 to 1300 degrees Fahr. (95 to 705 degrees Cent.) in steps of 200 degrees Fahr. (95 degrees Cent.). The results obtained demonstrated that tensile strength increases with heating to 570 degrees Fahr. (300 degrees Cent.) in all but the 0.10 per cent carbon steels, and drops on heating to higher temperatures.

In 1929, A. Pomp and P. Poellein (2) studied the strength and structure of cold-rolled annealed strip subjected to different previous treatments. These studies were made on a 0.65 per cent carbon steel that was cold-reduced up to 80 per cent and then annealed at 400, 480, 750, 1020, 1100, and 1200 degrees Fahr. (205, 250, 400, 550, 595, and 650 degrees Cent.). This steel showed a hardening up to a 480 degrees Fahr. (250 degrees Cent.) anneal, followed by a gradual softening at higher temperatures.

The work of Nead, Mahlie, and Dittrich (3) indicated that critical strain for a 0.05 per cent carbon strip varied with the hot mill finishing temperature. The now well established coarse crystallization phenomenon that occurs after cold reducing approximately 10 per cent and annealing at 1200 degrees Fahr. (650 degrees Cent.) was clearly shown. This same observation was brought out by

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

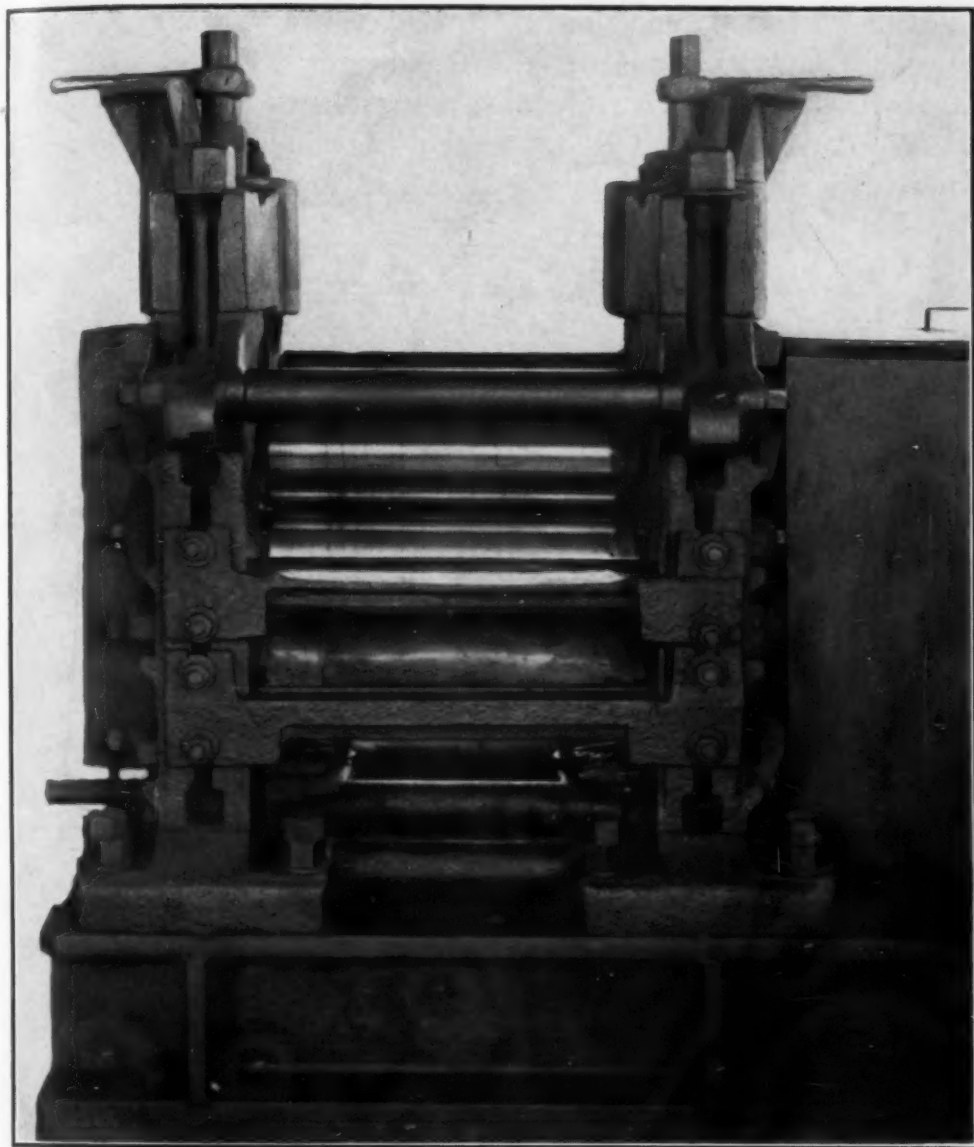


Fig. 1—View of Laboratory Experimental Rolling Mill.

A. Pomp (4), in 1934, in his studies made on a 1.2 per cent carbon steel. The steel was cold-worked within the 5 to 15 per cent range and annealed at 1290 degrees Fahr. (700 degrees Cent.). Pronounced grain coarsening was observed after this treatment.

In 1936, Hayes and Burns (5) studied the properties of mild steel sheets cold-reduced up to 60 per cent and annealed at 1100 and 1350 degrees Fahr. (595 and 730 degrees Cent.). Their studies showed that for 1100 degrees Fahr. (595 degrees Cent.) annealing treatment, hardness, yield point, and tensile strength increase with

percentage of cold reduction up to the critical strain region lying between 5 and 10 per cent. C. A. Edwards, D. L. Phillips, and W. H. E. Gullick (6) corroborated the results of Hayes and Burns.

W. P. Wallace and R. L. Rickett (7) studied the relationship between the amount of cold reduction and grain coarsening on an-

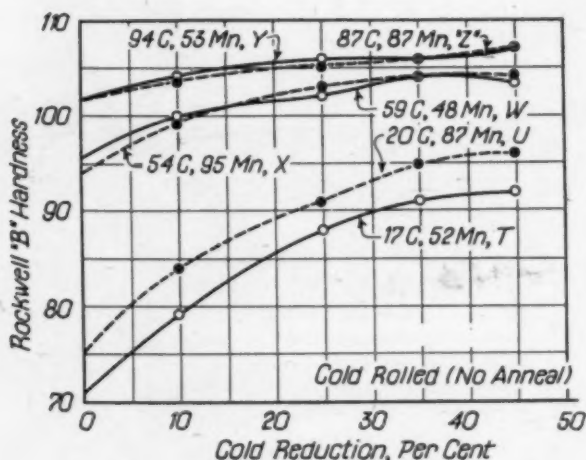


Fig. 2—Hardness Values of Steels Cold-Rolled (No Anneal). See Table III.

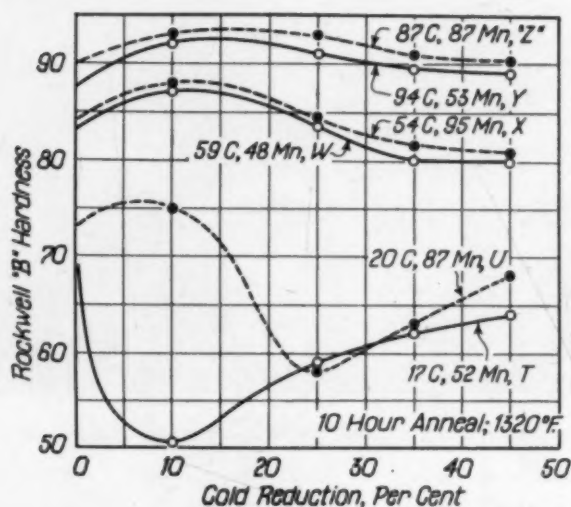


Fig. 3—Hardness Values on Steels Cold-Rolled. 10-Hour Anneal at 1320 Degrees Fahr. See Table III.

nealing at different temperatures. This included low carbon rimmed, aluminum-killed, and silicon-killed steels.

It was significant to note that in many of the foregoing investigations, the grain size of the steel studied was unknown. It is felt that, in some instances, differences in results obtained might be directly associated with differences in grain size of the material tested.

SELECTION OF STEELS

The steels selected for testing were such that two steels similar in carbon, but having different manganese contents, could be compared. An effort was made to obtain standard grades of steel, inso-

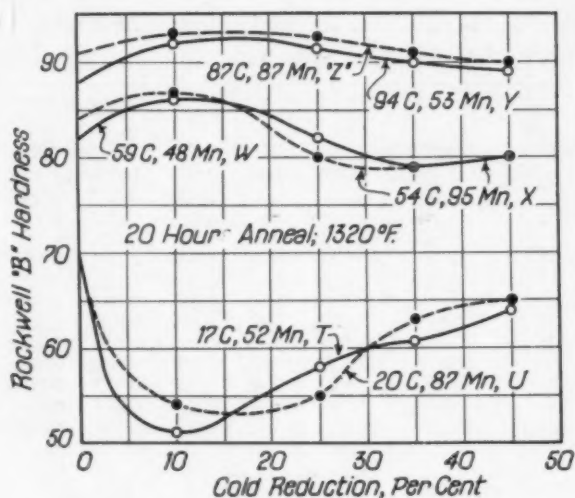


Fig. 4—Hardness Values on Steels Cold-Rolled. 20-Hour Anneal at 1320 Degrees Fahr. See Table III.

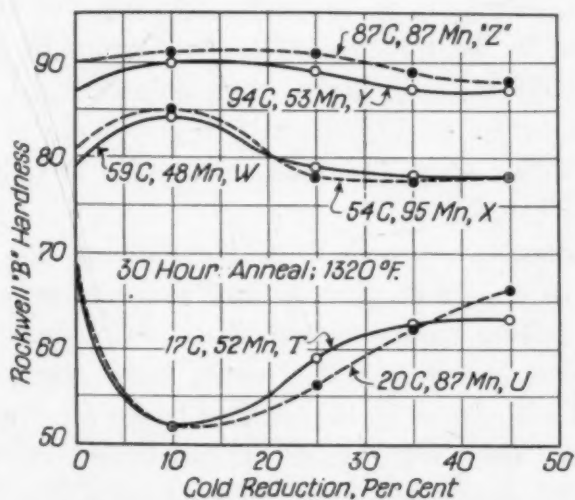


Fig. 5—Hardness Values on Steels Cold-Rolled. 30-Hour Anneal at 1320 Degrees Fahr. See Table III.

far as was possible. The heats selected were produced in accord with fine-grained melting practice, and were made in 135-ton open-hearth furnaces. The ladle analysis of the heats and check analysis on the strip, together with the tentative A.I.S.I. specification to which each approximately conforms, are tabulated in Table I. A code let-

ter was assigned to each steel and will be used hereinafter throughout this investigation report.

A standard McQuaid-Ehn grain size test was run on each of the above mentioned steels. All showed an austenite grain size within the $\frac{5}{8}$ range required for fine-grained material.

Table I

Code	Tentative Approx. A.I.S.I. No.	Analysis	C	Mn	P	S	Si	Cu	Cr	Ni
T	C-1017	Ladle	0.16	0.48	0.017	0.030	0.22
T		Strip	0.17	0.52	0.022	0.030	0.20	0.02	0.04	0.02
U	C-1019	Ladle	0.18	0.83	0.015	0.027	0.11
U		Strip	0.20	0.87	0.014	0.026	0.11	0.02	0.03	0.01
W	Non-Std.	Ladle	0.58	0.44	0.021	0.035	0.23
W		Strip	0.59	0.48	0.021	0.035	0.22	0.01	0.05	0.01
X	C-1055	Ladle	0.54	0.90	0.018	0.037	0.19
X		Strip	0.54	0.95	0.019	0.033	0.19	0.01	0.04	0.01
Y	C-1095	Ladle	0.90	0.50	0.015	0.033	0.15
Y		Strip	0.94	0.53	0.017	0.032	0.15	0.02	0.08	0.01
Z	C-1084	Ladle	0.85	0.82	0.023	0.029	0.14
Z		Strip	0.87	0.87	0.021	0.027	0.14	0.02	0.05	0.01

PROCEDURE

In order that all tests could be made on material of approximately the same gage thickness, it was necessary to normalize at the proper intermediate gage thickness to give the desired amount of cold reduction to the finished strip. For example, steel "T" was normalized at 0.085 inch thickness, then cold-reduced to 0.047 inch to give a cold reduction of 45 per cent; to give 0 per cent cold reduction, another piece of strip "T" was normalized at 0.047 inch thickness and was so tested.

This procedure was used as a convenience in obtaining the desired amount of cold reduction as well as a uniform finished strip thickness. Hot rolling to the intermediate strip sizes prior to final cold reduction was considered but would have required many mill changes that did not appear to be justified based on preliminary tests. These preliminary tests were made on hot-rolled, cold-reduced and annealed strip with various amounts of cold reduction and to several different final gage thicknesses. The results of these tests agreed in every respect with the findings of this investigation herein reported. Likewise, numerous tests on commercial production material gave comparable results, indicating the validity of the testing procedure.

Normalizing was carried out at 1700 degrees Fahr. (925 degrees Cent.) for $\frac{1}{2}$ hour at heat. The normalizing temperature of 1700 degrees Fahr. (925 degrees Cent.) was selected to simulate regular

rolling mill finishing temperatures. Microscopic comparison of normalized and hot-rolled strip showed similar microstructures indicating comparable conditions.

Cold rolling was accomplished by passing strip samples between the rolls of a small three-high laboratory experimental mill, shown in Fig. 1.

The hot-rolled strip size, the thickness after various amounts of reduction, and final cold-rolled size are tabulated in Table II.

Table II

Code	Hot Rolled Strip Size in Inches	Thickness in Inches of Normalized Strip and Per Cent Final Cold Reduction					Final Cold-Rolled Strip Size in Inches
		0%	10%	25%	35%	45%	
T	2 x 0.085	0.047	0.053	0.062	0.072	0.085	2 x 0.047
U	1 $\frac{3}{4}$ x 0.081	0.045	0.050	0.059	0.069	0.081	1 $\frac{3}{4}$ x 0.045
W	1 $\frac{1}{8}$ x 0.085	0.047	0.053	0.062	0.072	0.085	1 $\frac{1}{8}$ x 0.047
X	1 $\frac{3}{4}$ x 0.081	0.045	0.050	0.059	0.069	0.081	1 $\frac{3}{4}$ x 0.045
Y	2 $\frac{7}{8}$ x 0.084	0.046	0.052	0.061	0.071	0.084	2 $\frac{7}{8}$ x 0.046
Z	1 $\frac{3}{4}$ x 0.075	0.041	0.046	0.054	0.063	0.075	1 $\frac{3}{4}$ x 0.041

Table III

Rockwell "B" Hardness of Strip After Cold Rolling and Box Annealing as Indicated

Code	Chemistry		Reduction Per Cent	Box Annealing Time at 1320 Degrees Fahr.			
	Carbon Per Cent	Manganese Per Cent		0 Hour	10 Hours	20 Hours	30 Hours
T	0.17	0.52	0	71	68	69	68
			10	79	50.5	51	52
			25	88	59	58	58
			35	91	62	61	62
			45	92	64	64	63
U	0.20	0.87	0	75	73	68	69
			10	84	75	54	52
			25	91	58	55	56
			35	95	63	63	62
			45	96	68	65	66
W	0.59	0.48	0	95.5	83	82	79
			10	100	87	86	84
			25	102	84	82	79
			35	104	80	79	78
			45	103.5	80	80	78
X	0.54	0.95	0	94	84	84	81
			10	99	88	87	85
			25	103	84	80	78
			35	104	82	79	78
			45	104	81	80	78
Y	0.94	0.53	0	102	88	88	87
			10	103.5	92	92	90
			25	106	91	91	89
			35	106	90	90	87
			45	107	89	89	87
Z	0.87	0.87	0	102	90	91	90
			10	103.5	93	93	91
			25	105	93	92	91
			35	106	90.5	91	89
			45	107	90.5	90	88

After cold reduction, samples were annealed at 1320 degrees Fahr. (715 degrees Cent.) for 10, 20, 30 hours. In order to minimize surface decarburization during annealing, all samples were wrapped in "waster sheets" and sealed in air-tight containers. Annealing was accomplished in a small Westinghouse Electric Furnace

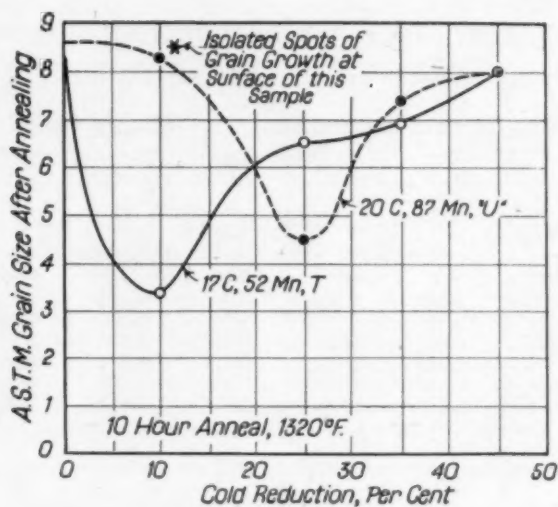


Fig. 6—A.S.T.M. Grain Size After Cold Rolling and Annealing for 10 Hours at 1320 Degrees Fahr.

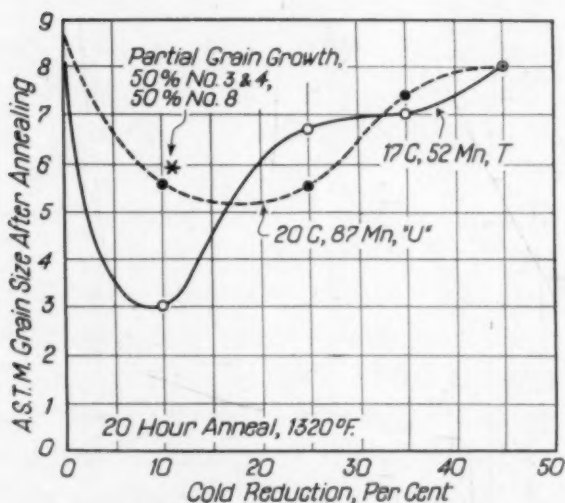


Fig. 7—A.S.T.M. Grain Size After Cold Rolling and Annealing for 20 Hours at 1320 Degrees Fahr.

having Leeds and Northrup automatic temperature control. As a check, a platinum-rhodium thermocouple was inserted immediate to the work to measure accuracy of automatic temperature control.

HARDNESS RESULTS

The hardness obtained on the several steels after various amounts of prior cold reduction and annealing times are tabulated in Table III.

All hardness values are the average of three readings.

The hardness values recorded in Table III are shown in graph form in Figs. 2, 3, 4, and 5. Previous investigators, (1), (2), (5),

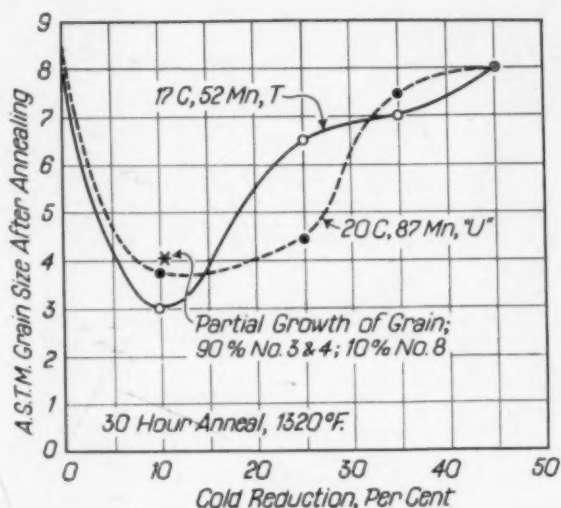


Fig. 8—A.S.T.M. Grain Size After Cold Rolling and Annealing for 30 Hours at 1320 Degrees Fahr.

(7), have shown quite similar results although the effect of time at the annealing temperature was not so completely exploited as in the present work.

It is significant to note that an increase in hardness was obtained in the intermediate and high carbon steels after cold rolling 10 per cent and annealing as compared to material that was similarly annealed but had received no cold reduction. This hardness increase effect was also observed in the low carbon, high manganese steel after a 10-hour anneal. This observation can be explained as follows:

In annealing cold-rolled material, there are two physical changes that take place within the metal. They are: (A) recrystallization of the severely elongated grains to uniform equiaxed grains, and (B) a gradual spheroidization of the pearlitic carbide; both changes effecting a lowering of the original hardness. The increase in hardness noted at 10 per cent reduction was probably due to an insufficient amount of reduction to cause recrystallization and its accompanying

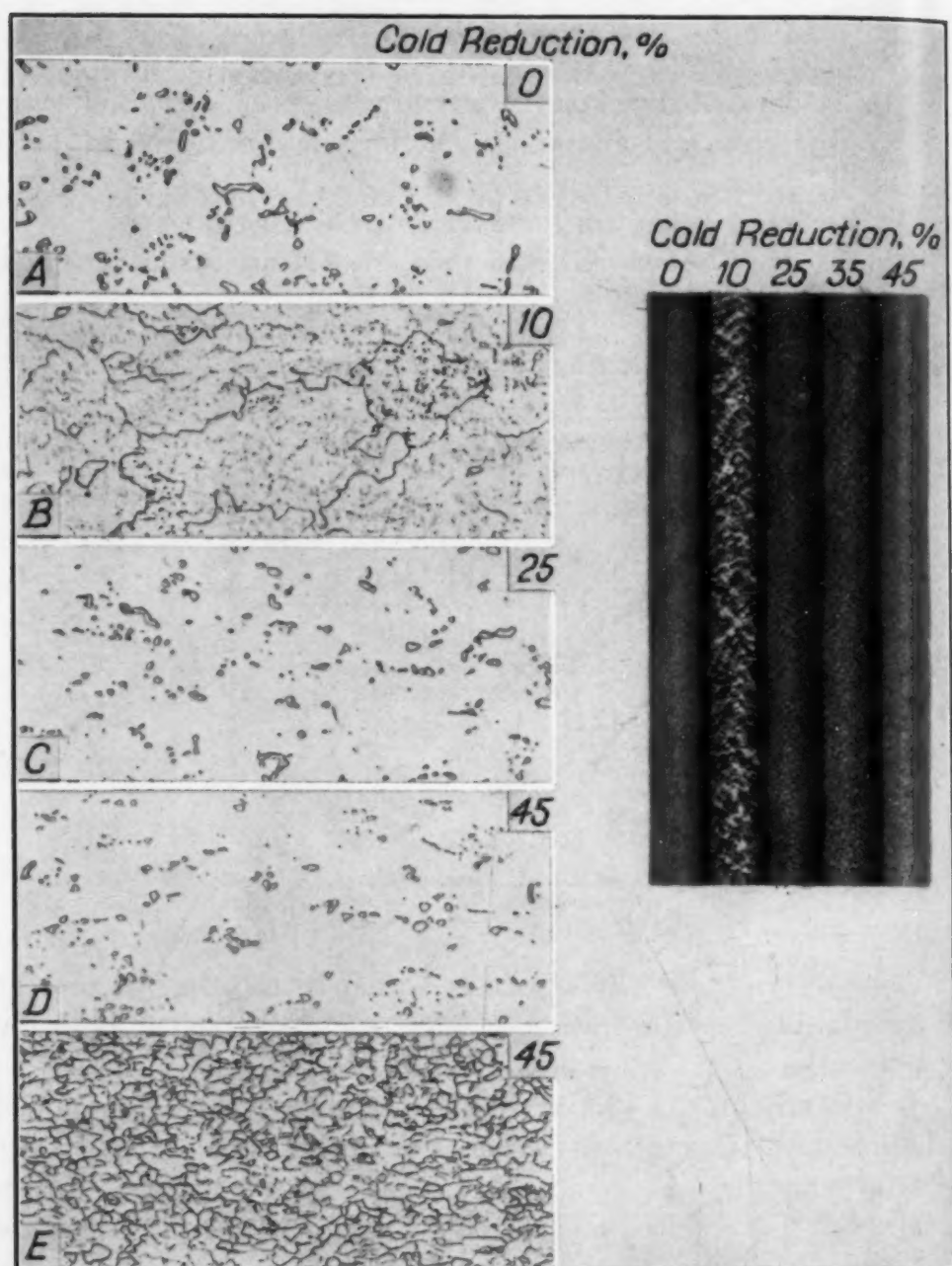


Fig. 9—Photomicrographs and Photographs of Cold Bend Tests on Steel "T" Annealed 1320 Degrees Fahr. for 10 Hours. A, C and D Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. B and E Photomicrographs of Grain Size. $\times 100$. 4 Per Cent Nital. Bend Test Photographs $\times 2$.

softening during annealing. Concomitantly, the amount of spheroidization at 10 per cent reduction was insufficient to reduce the hardness increase that was introduced in the metal by the cold reduction. Microscopic examination substantiated this theory.

The drop in hardness noted on the low carbon steels at 10 per

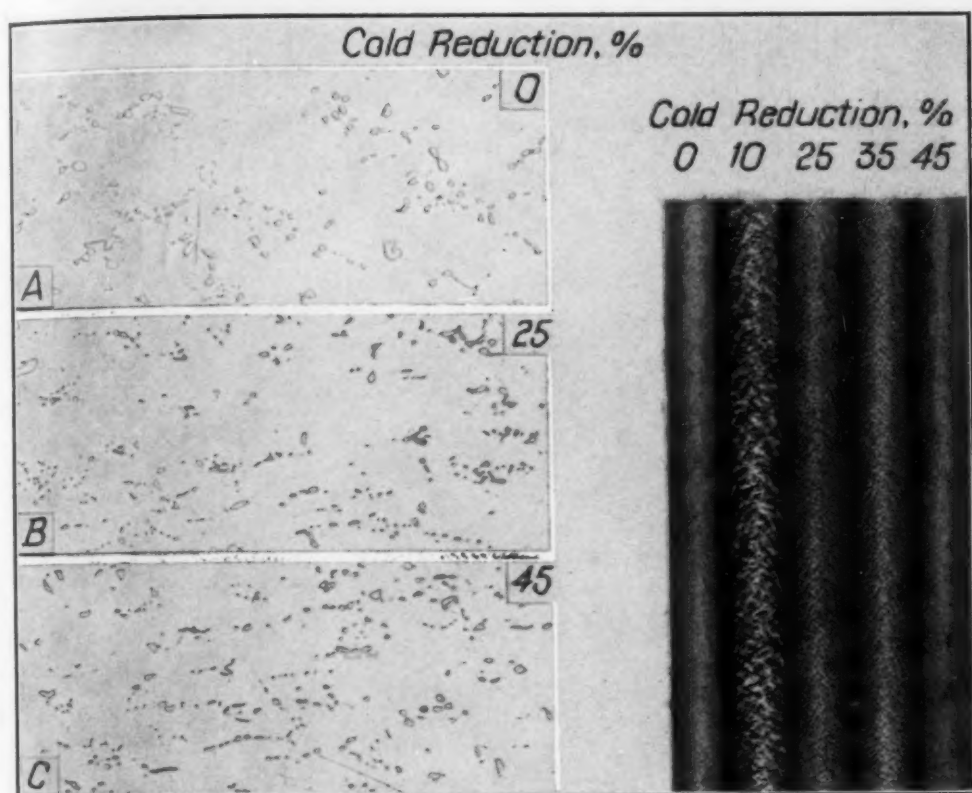


Fig. 10—Photomicrographs and Photographs of Cold Bend Tests on "T" Annealed 1320 Degrees Fahr. for 30 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 2$.

cent reduction is directly related to the recrystallized grain size after annealing. At 10 per cent reduction a very coarse grain size resulted after annealing with its accompanying low hardness value. This observation agrees with the work of previous investigators, notably W. P. Wallace and R. L. Rickett (7).

In Figs. 6, 7, and 8, grain size is plotted against per cent of cold work. It will be noted, by comparing these curves with Figs. 3, 4, and 5, that the hardness is directly related to the recrystallized grain size. Steel "U" was not as susceptible to grain coarsening as steel "T", which feature may be associated with the higher manganese content.

MICROSCOPIC EXAMINATION

Micro specimens were taken from each of the steels after cold reducing 0, 10, 25, 35, and 45 per cent and annealing for 10, 20, and 30 hours at temperature. The photomicrographs, Figs. 9 to 20, inclusive, depict the microstructures obtained with various percentages

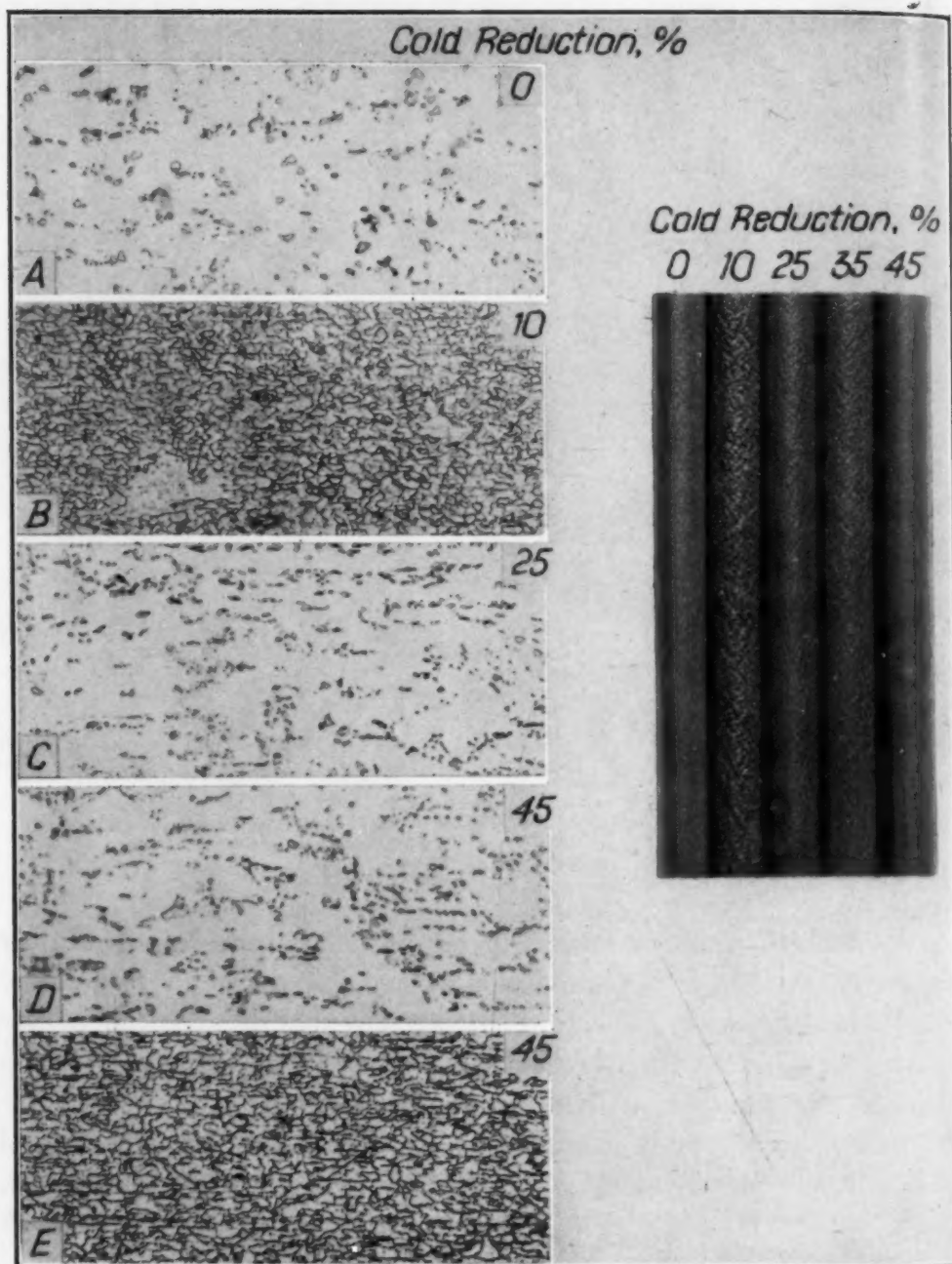


Fig. 11—Photomicrographs and Photographs of Cold Bend Tests on Steel "U" Annealed 1320 Degrees Fahr. for 10 Hours. A, C and D Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. B and E Photomicrographs of Grain Size. $\times 100$. 4 Per Cent Nital. Bend Test Photographs $\times 2$.

of reduction and different annealing times. The progressive spheroidization of the carbide as the amount of cold work is increased, particularly in the intermediate and high carbon steels, can readily be observed from these photomicrographs. The structures at 10 and 35 per cent reduction, as well as after the 20-hour anneal, were not

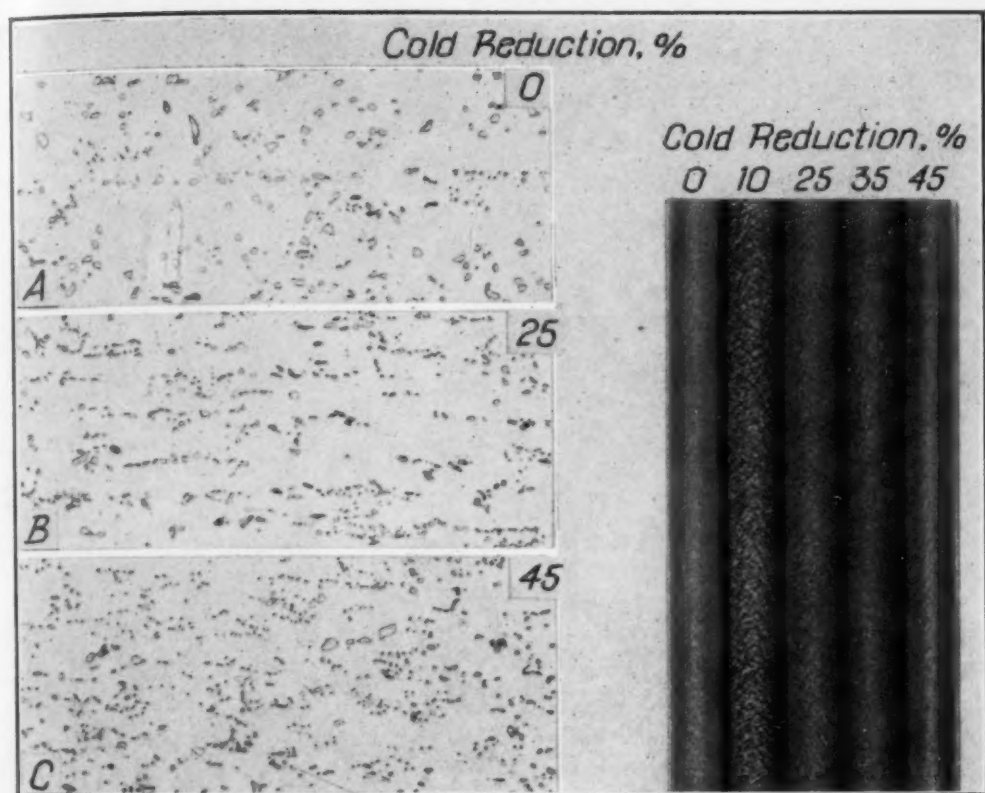


Fig. 12—Photomicrographs and Photographs of Cold Bend Tests on Steel "U" Annealed 1320 Degrees Fahr. for 30 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 2$.

shown in all cases, to minimize the number of photomicrographs.

The grain size of the low and intermediate carbon steels was determined after cold reduction and annealing. The photomicrographs taken after 10 per cent cold reduction and annealing on the low and intermediate carbon steels, Figs. 9, 11, and 13, clearly show the grain coarsening that occurred due to the critical strain induced by cold rolling. Heavy amounts of prior cold reduction completely eliminated grain coarsening during annealing, as shown by photomicrographs of suitably etched samples taken on material cold-rolled 45 per cent and annealed, Figs. 9, 11, and 13. We were unable to determine accurately the grain size of the high carbon steels after annealing because of masking of the grain boundaries by the spheroidized carbides and partially dissociated pearlite.

BEND TESTS

All strip samples were subjected to longitudinal cold bend tests. The low carbon steels "T" and "U", and the intermediate carbon

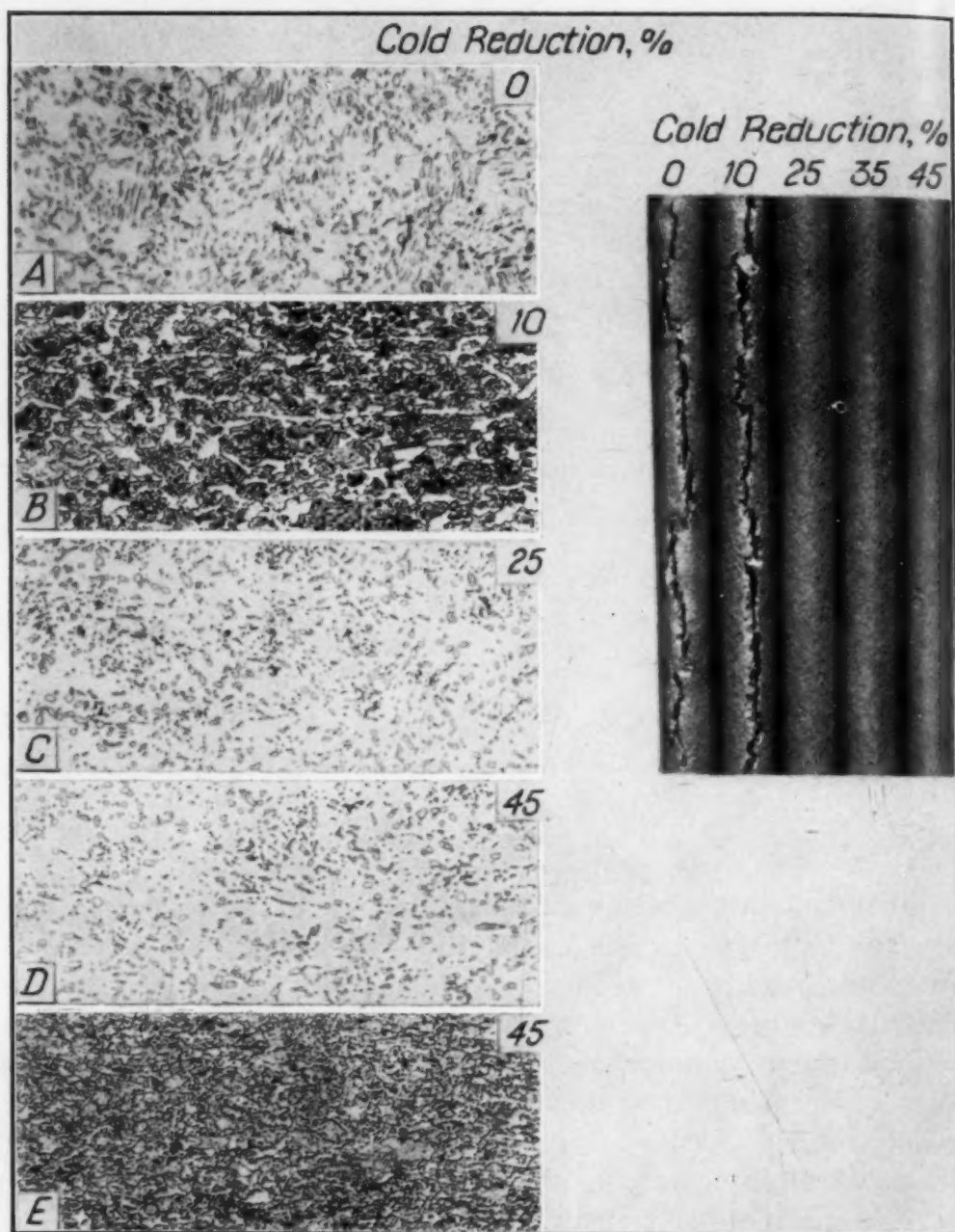


Fig. 13—Photomicrographs and Photographs of Cold Bend Tests on Steel "W" Annealed 1320 Degrees Fahr. for 10 Hours. A, C and D Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. B and E Photomicrographs of Grain Size. $\times 100$. 4 Per Cent Nital. Bend Test Photographs $\times 2$.

steels "W" and "X", were bent flat on themselves under a pressure of 20,000 pounds. Uniform pressure was assured in every case by placing samples, that had been previously partially bent in a hand vise, between parallel plates of a Baldwin-Southwark tensile test machine that was loaded in compression.

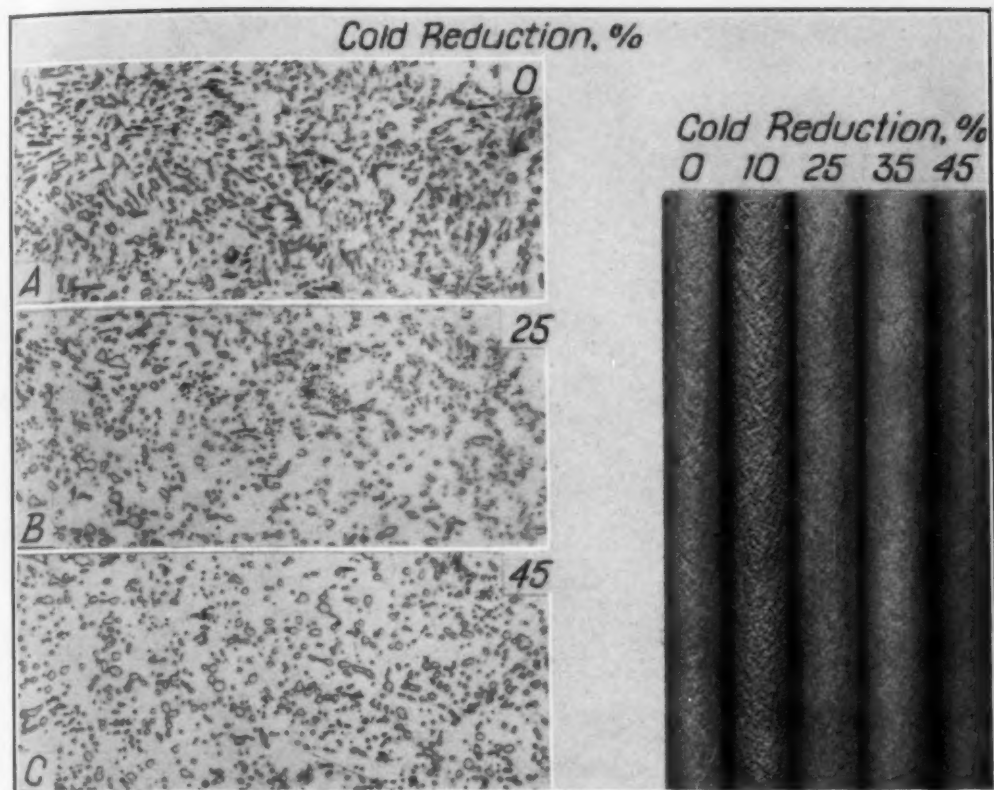


Fig. 14—Photomicrographs and Photographs of Cold Bend Tests on Steel "W" Annealed 1320 Degrees Fahr. for 30 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 2$.

The high carbon steels "Y" and "Z" were bent on a radius equal to two times their final gage thickness. This degree of cold bending was selected because neither of the high carbon steels, under any test condition, would withstand a longitudinal flat bend test. Furthermore, bending on a radius equal to two times the thickness produced the proper amount of stress in the outer fibers to show differences in the response of the material to fracturing.

The results of the bend tests are shown graphically in Figs. 21, 22, 23, 24, 25, and 26. Annealing times are plotted against the per cent of cold reduction. The extent of cracking is indicated and rated as heavy, light, or incipient cracks, and satisfactory bends (free from cracks).

Heavy cracks are those very easily visible to the eye, whereas light or incipient cracks are those barely discernible. This rating method is clarified by the photomicrographs taken of the bend test samples. These are shown in Figs. 9 to 20, inclusive. The degree of fracturing illustrated can be compared to the empirical rating assigned to the particular sample on the graph.

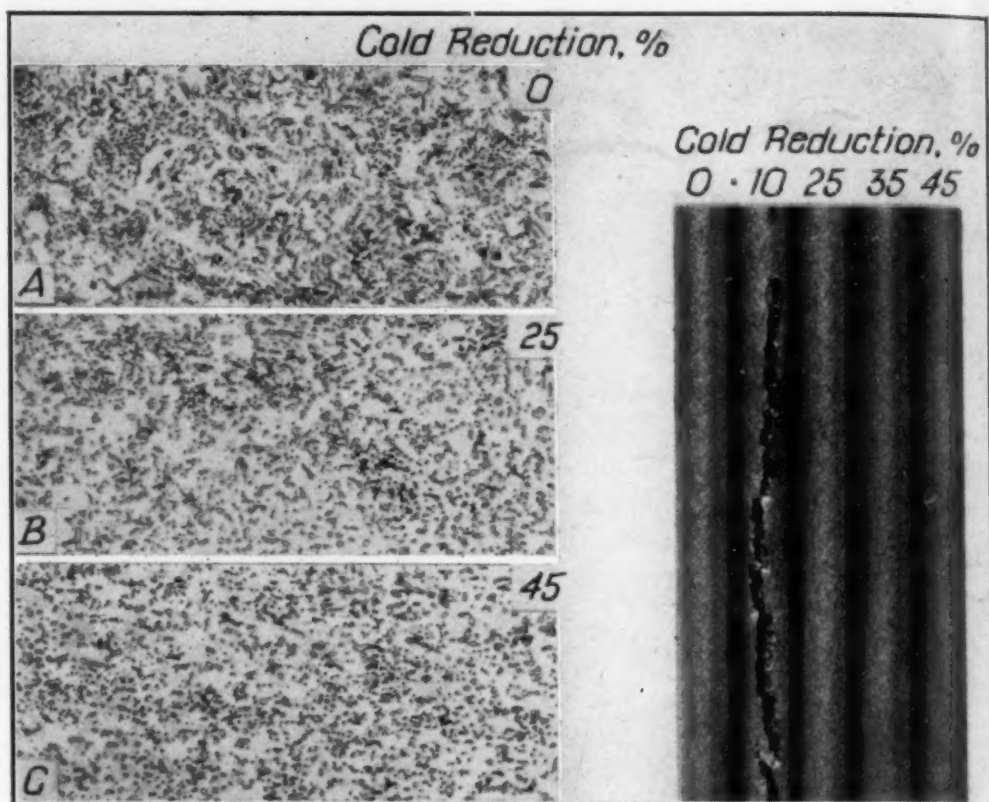


Fig. 15—Photomicrographs and Photographs of Cold Bend Tests on Steel "X" Annealed 1320 Degrees Fahr. for 10 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 2$.

The low carbon steels "T" and "U" all gave satisfactory longitudinal flat bends. Grain coarsening after 10 per cent prior cold reduction is clearly shown in both steels.

On the intermediate carbon steels, "W" and "X", the effect of the annealing time and amount of cold reduction prior to anneal is clearly shown in Figs. 23 and 24. Exemplary cold bend tests from which these curves were plotted are shown in the photomicrographs, Figs. 13, 14, 15, and 16. On the graphs, fields wherein heavy cracks, light cracks, incipient cracks and no cracks were obtained, are separated by empirical curves.

It is interesting to note on steel "W" that satisfactory bends were realized on the normalized sample after a 30-hour anneal. This was not true of steel "X" which had essentially the same chemical composition as "W", with the exception of a higher manganese content. The exact effect of increased manganese content on bend tests was not clearly brought out in these tests but appeared to favor the lower manganese content.

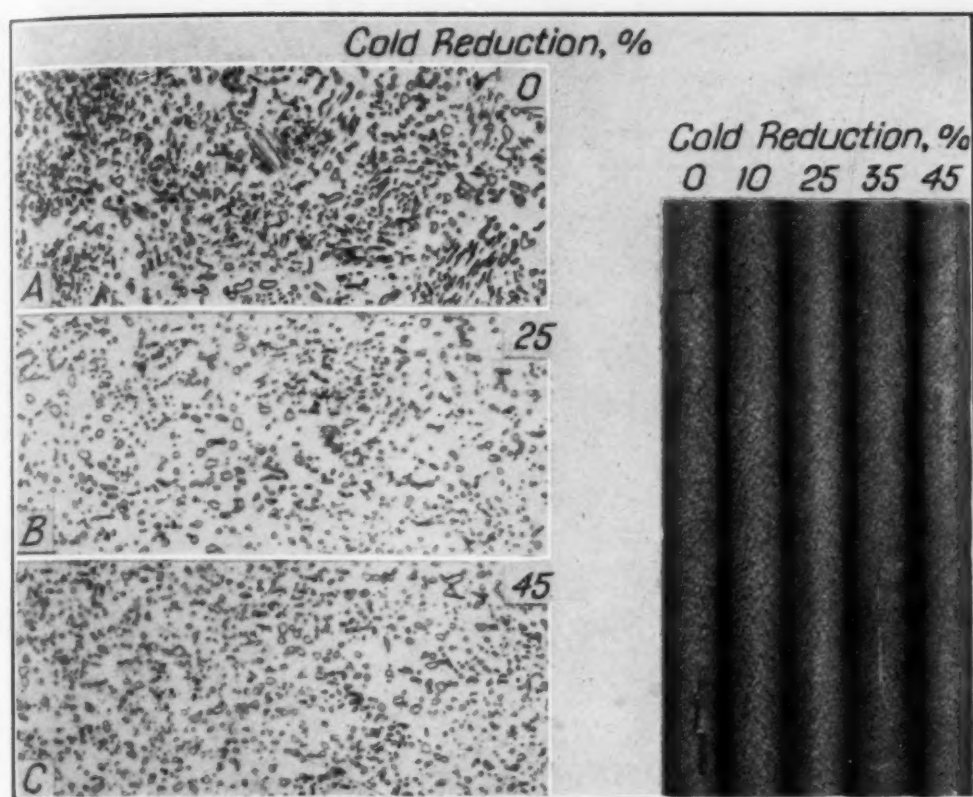


Fig. 16—Photomicrographs and Photographs of Cold Bend Tests on Steel "X" Annealed 1320 Degrees Fahr. for 30 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 2$.

In both intermediate carbon steels, the amount of prior cold reduction materially reduced the annealing time required to obtain satisfactory flat bends. Both steels were satisfactory after a 10-hour anneal with a minimum of 35 per cent prior cold reduction. Increased percentages of cold reduction also resulted in smoother bends for a given annealing time.

The results of bend tests on steels "Y" and "Z" are shown graphically in Figs. 25 and 26, respectively. On these two eutectoid steels it was found that no samples, regardless of the amount of prior cold reduction or time of anneal, would withstand a longitudinal flat bend test without showing heavy, and in most cases complete, cracking. Consequently, in order to show differences in the materials' response to the bend test, it was necessary to bend all samples on a radius equal to two times the thickness of the cold-rolled, annealed strip.

Steel "Y" gave satisfactory bends after cold reducing 35 per cent with a 30-hour anneal and after 45 per cent cold reduction with 10,

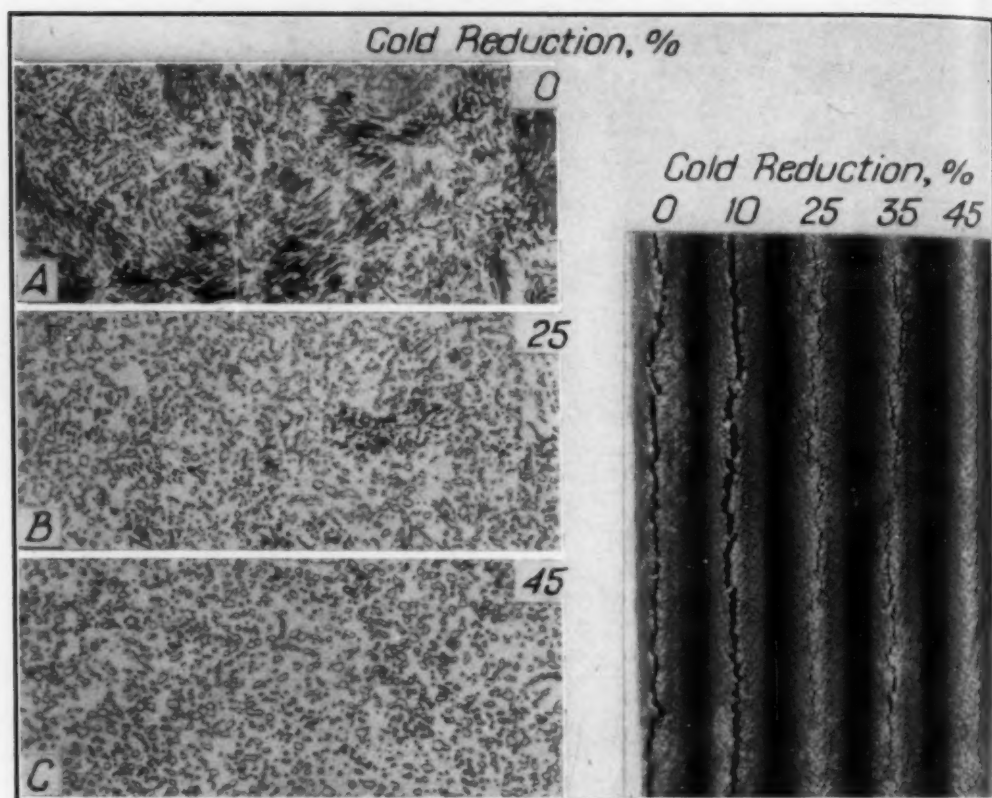


Fig. 17—Photomicrographs and Photographs of Cold Bend Tests on Steel "Y" Annealed 1320 Degrees Fahr. for 10 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 1$.

20, and 30-hour anneals. All other combinations of cold reduction and annealing times resulted in unsatisfactory bends.

Steel "Z" gave a satisfactory bend only after the 30-hour anneal with 45 per cent prior cold reduction. Material from steel "Z" was also given 55 per cent cold reduction. Satisfactory bends were obtained after 20 and 30-hour anneals on this material cold-reduced 55 per cent. The 10-hour anneal was insufficient to give satisfactory cold bends even after cold reducing 55 per cent previously.

SUMMARY

An investigation was made to study the effect of the amount of prior cold reduction and annealing times on longitudinal bends on six types of fine-grained plain carbon steels. The types selected for testing were low carbon (0.15 to 0.20 per cent), intermediate carbon (0.50 to 0.60 per cent), and eutectoid carbon (0.85 to 0.95 per cent). Low and high manganese content in each type was compared. *All strip samples* were normalized from 1700 degrees Fahr. (925 degrees

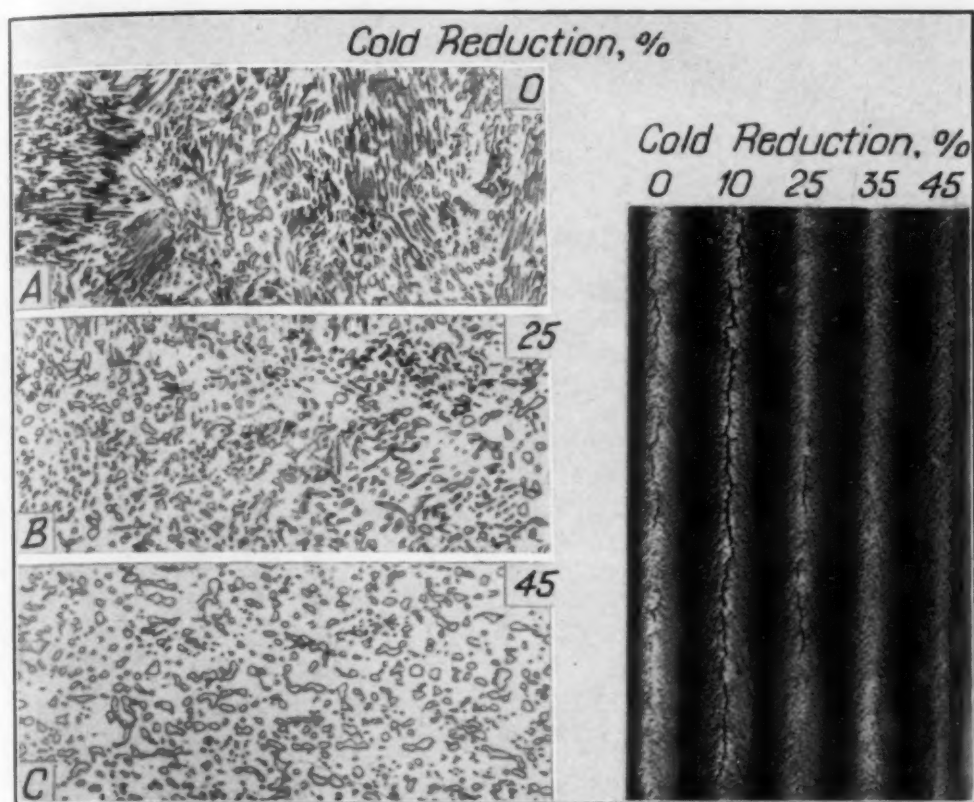


Fig. 18—Photomicrographs and Photographs of Cold Bend Tests on Steel "Y" Annealed 1320 Degrees Fahr. for 30 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 1$.

Cent.) to obtain structural uniformity before cold reducing. The gage thickness in all cold-rolled strip tested was practically constant, ranging from 0.041 to 0.047 inch.

The Rockwell hardness of steels "T" and "U" after cold reducing and annealing was found to be directly related to the recrystallized grain size. On the intermediate and high carbon steels, a slight increase of hardness was noted at 10 per cent reduction after all annealing times studied. With increased percentages of cold reduction the hardness was gradually lowered for all annealing times. For a given percentage of cold reduction increased annealing times lowered the hardness. Given a constant annealing time, increasing percentages of cold reduction lowered the hardness.

Microscopic examination disclosed accelerated spheroidization of the carbide with increasing amounts of cold reduction prior to the anneal. The well known grain coarsening phenomenon that occurs on low carbon steels after small amounts of cold reduction and annealing was observed. Some coarsening of the grain size was even evident

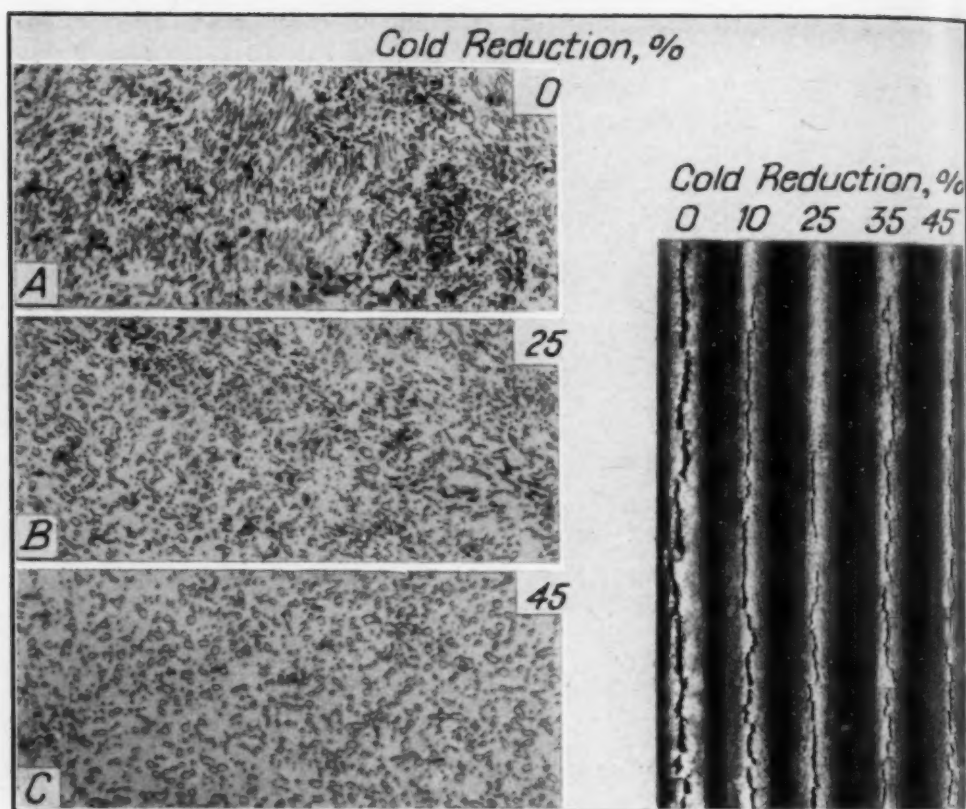


Fig. 19—Photomicrographs and Photographs of Cold Bend Tests on Steel "Z" Annealed 1320 Degrees Fahr. for 10 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 1$.

after 25 and 35 per cent reductions on these two steels. Satisfactory response to cold bending could not be conclusively predicted in every case from the appearance of the microstructure or hardness of the intermediate and high carbon steels. The trend was toward improved longitudinal bends with increased agglomeration and uniform dispersion of the carbide.

Longitudinal flat bends were made on the low and intermediate carbon steels (T, U, W, X). Complete breaks resulted when longitudinal flat bends were tried on the high carbon steels (Y and Z). These were bent longitudinally on a radius equal to two times their gage thickness.

Satisfactory bends were obtained on the low carbon steels (T and U) regardless of the amount of prior cold reduction or annealing time. "Orange peel" surface resulting from grain coarsening was observed on bend samples that had small amounts of cold reduction prior to annealing.

On the intermediate carbon steels (W and X) satisfactory flat

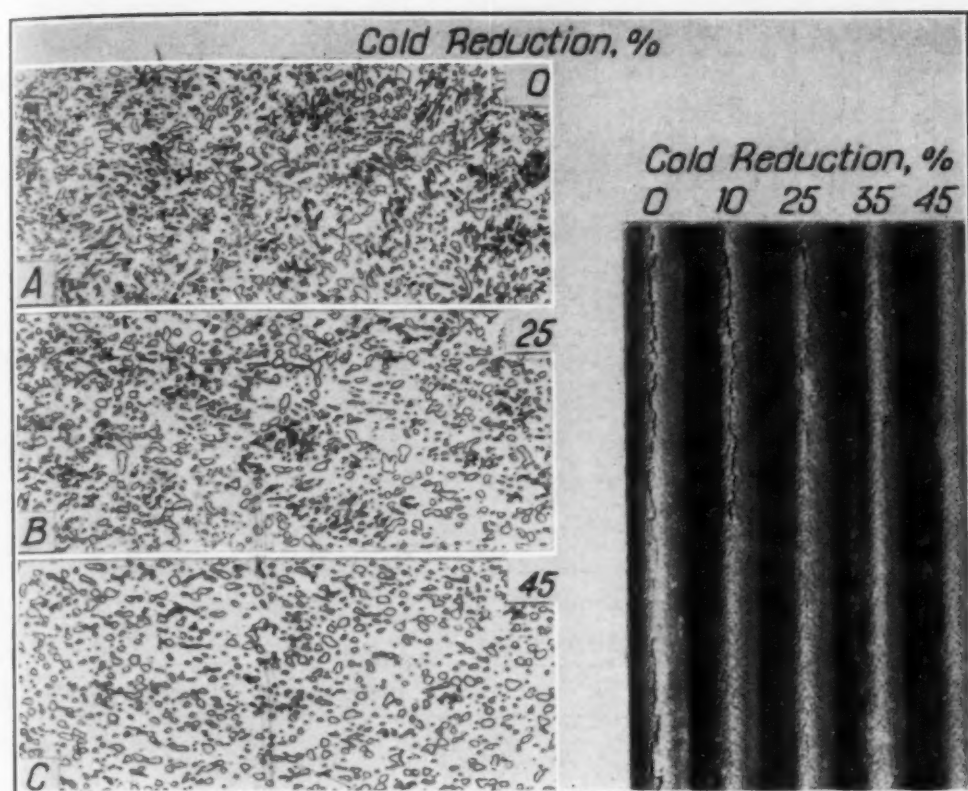
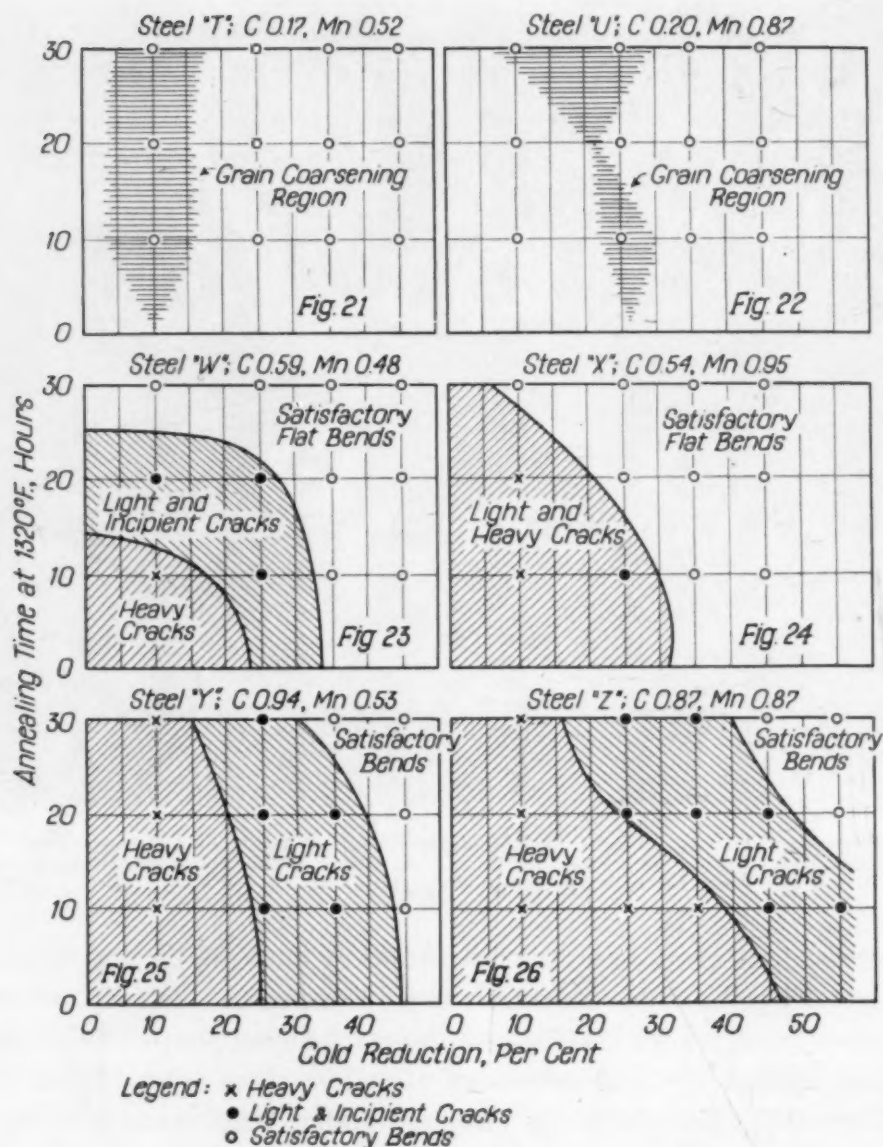


Fig. 20—Photomicrographs and Photographs of Cold Bend Tests on Steel "Z" Annealed 1320 Degrees Fahr. for 30 Hours. A, B and C Photomicrographs of Carbide. $\times 500$. 4 Per Cent Picral. Bend Test Photographs $\times 1$.

bends resulted from an annealing time of only 10 hours when the amount of prior cold reduction was a minimum of 35 per cent. Freedom from cracks resulted on the normalized strip, "W", after a 30-hour anneal. It was necessary to cold-reduce steel "X" a minimum of 10 per cent before a satisfactory flat bend could be obtained after a 30-hour anneal.

On the high carbon steels (Y and Z), longitudinal flat bends resulted in heavy cracks regardless of the amount of prior cold reduction or annealing time. Satisfactory longitudinal bends made on a radius equal to two times the thickness of the strip were produced on steel "Y" after 45 per cent prior cold reduction, irrespective of the annealing times employed. Steel "Z" gave a satisfactory bend on a radius equal to two times the strip thickness only after a 30-hour anneal and 45 per cent previous cold reduction. When cold-reduced 55 per cent, steel "Z" gave satisfactory bends after both 20 and 30-hour annealing periods; but light cracks developed after the 10-hour anneal.



Figs. 21-26—Bend Tests Shown Graphically. Annealing Times are Plotted Against the Per Cent of Cold Reduction.

CONCLUSIONS

Heavy amounts of cold reduction are helpful in accelerating the spheroidization of the carbide and improving the satisfactory response of strip steel to longitudinal bend tests after annealing. Killed, fine-grained, low carbon (0.15 to 0.20 per cent) and intermediate carbon (0.50 to 0.60 per cent) steels up to 0.045 inch gage thickness will withstand a longitudinal flat bend test without cracking when properly cold-rolled and annealed.

Eutectoid carbon steels (0.85 to 0.95 per cent) will crack on a longitudinal flat bend test in the gage thickness tested (0.041 to 0.046 inch). These can be bent satisfactorily on a radius equal to two times the gage thickness with sufficient prior cold rolling and annealing.

An accurate prediction of a material's response to the bend test could not, in every case, be based on the hardness or the appearance of the annealed microstructure. In general, a fine but uniformly spheroidized condition of the carbide gave the best results.

Increasing the manganese content had little effect on the low carbon steels, except to diminish slightly the tendency toward exaggerated grain growth after small amounts of cold rolling and annealing. In the intermediate and high carbon steels, the lower manganese content appeared to improve the material's response to the bend test. However, the many factors influencing the test made the isolation of each contributing factor extremely difficult, and suggest the need for further work for verification of this important point.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance and suggestions of Mr. R. M. Crigler and Mr. E. N. Hibbert, of Carnegie-Illinois Steel Corporation, Youngstown Metallurgical Department, in the development of certain information given in this paper. Likewise, the help of our Bureau of Information and Tests, Pittsburgh Metallurgical Department, in reviewing the literature and preparation of graphs, is gratefully acknowledged. For permission to publish this work, the authors wish to thank the management of the Carnegie-Illinois Steel Corporation.

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7. W. P. Wallace and R. L. Rickett, "Influence of Annealing Temperature, Annealing Time and Amount of Prior Cold Reduction on the Hardness and Microstructure of Low Carbon Rimmed, Aluminum-Killed and Silicon-Killed Steels," United States Steel Corporation Research Laboratory Report No. 369, May 10, 1939.

DISCUSSION

Written Discussion: By W. A. Carlson, assistant manager, and W. L. Keene, manager, Metallurgical Department, Superior Steel Corp., Carnegie, Pa.

The authors are to be complimented for the excellent way in which they presented their findings on this very interesting but hitherto neglected subject. It is gratifying to have our own very general observations confirmed by this careful and detailed investigation. We have also found that a higher hardness is obtained if strip is given a light reduction (10 per cent) before annealing than is obtained by annealing hot-rolled (or normalized) material for the same time at the same temperature.

We were somewhat surprised to note the effect of annealing time on steel (U) (0.20 carbon, 0.87 manganese) after a 10 per cent cold reduction. It is shown that a 10-hour anneal caused a slight increase in hardness with no grain coarsening whereas the 20- and 30-hour anneals definitely increased the grain size and lowered the hardness. It has been our experience that on steels subject to critical grain growth, the amount of cold work and the annealing temperature were by far more important factors than time at temperature. We feel that in most cases, practically all the critical grain growth will take place in the first few hours at temperature and that extended annealing times would not change the final result to any particular degree.

The authors have concluded, and rightly so, in our opinion, that both increasing amounts of cold work prior to annealing, and increasing time at temperature during annealing, are helpful in developing maximum ductility as shown by the bend test. This brings up an interesting question, however, and we would like the authors' opinion. Suppose, for instance, in the case of the medium and high carbon steels, the total reduction and total annealing time be broken up into more than one operation, how would the finished products compare as regards microstructure, hardness and bending characteristics? Take the following concrete examples: Case 1—Hot roll 0.070 inch; cold roll to 0.045; anneal at 1320 degrees Fahr. (715 degrees Cent.) for 10 hours. Case 2—Hot roll 0.070 inch; cold roll to 0.063 inch; anneal 1320 degrees Fahr. (715 degrees Cent.) for 5 hours; cold roll to 0.045 inch; anneal 1320 degrees Fahr. (715 degrees Cent.) for 5 hours. In both cases the cold reduction is the same, and the time at annealing temperature is the same—would the final results be the same?

We agree with the authors that the size and dispersion of the carbides (in the high carbon steels) is perhaps more important as a measure of the bending characteristics of the material than the hardness values per se. We have had

cases wherein two pieces of steel, from the same heat, and of the same size and with the same hardness, treated the same way, would in one case bend flat and in the other, crack at around 90 to 135 degrees. The microstructure proved to be entirely different. This behavior can sometimes be traced back to hot mill practice.

Now that the authors have made such an excellent beginning to the study of an intensely practical problem, we would like to suggest that this work be carried even further. For instance, it would be interesting to obtain the tensile properties of the steels studied, especially to see what kind of correlation exists between the elongation values in tension and the elongation of the outer fibres in bending. It might be well to mention that the manner of performing bend tests is a very important factor in such a comparison and that this should be clearly described or else results of independent investigators are bound to differ considerably.

Written Discussion: By E. P. Beachum, Baltimore.

I have found the paper by Messrs. Sprankle and Hughes to be most interesting, and I think the authors are to be particularly commended for the excellent presentation of their conclusions in Figs. 21 to 26 inclusive. In many respects their conclusions have been verified in my own experience, although I am rather of the opinion that the transverse bend test may often be even more informative than the longitudinal one.

However, I should like to ask several questions:

First, in the present paper, are the authors of the opinion that prior fragmentation was completely eliminated by the normalizing, and was the same grain size and carbide distribution produced by the normalizing regardless of prior treatment?

Would similar results be expected from a rimming steel?

Extending the experimental results to a production problem, what would be the effect on the bending quality of a conventional cold-reduced and box annealed sheet, of the grain size and carbide condition produced in the hot-rolled band used by variation of hot mill practice; for example as between air cooling and water cooling on the run-out table and in the coiler?

Authors' Reply

We appreciate the comments and questions raised by Messrs. Carlson and Keene of the Superior Steel Corporation, and by Mr. Beachum, and will endeavor to answer the questions raised in the sequence in which they are listed.

Referring first to the questions by Messrs. Carlson and Keene, and specifically to the effect of annealing time on grain coarsening, we agree that the amount of cold rolling and the annealing temperature are more important than the actual time at temperature, but time at temperature also has an effect, especially where very light cold reduction is involved. Our studies show that the rate of grain coarsening will vary somewhat, depending upon the particular steel investigated. It should be noted from Fig. 6 that steel "U" showed isolated spots of grain growth after a 10-hour anneal, which became more pronounced after the 20- and 30-hour anneals. It is our belief that the 10 per cent reduction failed to produce marked "critical strain" necessary for pronounced

grain growth after a 10-hour anneal. Longer annealing times resulted in increased grain growth in both size and intensity. It should be emphasized that, where the amount of cold work is light, time at temperature must be taken into consideration in problems involving grain growth.

The question of satisfactory response to the bend test of materials having the same chemical composition, one of which was processed directly to the finished gage, the other being given an intermediate anneal, but both having finally the same amount of cold reduction from hot-rolled to cold-rolled strip, is an interesting case and one that has received attention both in laboratory and in actual production problems. Normally, the microstructures and hardnesses would be similar, although our laboratory work indicates that the material given the single reduction without intermediate anneal gives the better bend test. This conclusion is based on a comparatively few tests made in our laboratory and may possibly need further verification.

We were glad to note that these gentlemen concur with our findings to the effect that size and dispersion of the carbides in the high carbon steels are more important as a measure of bending characteristics than the hardness values. We agree that, in some instances, the prior structure resulting from rolling mill practice has a definite effect.

The manner in which the bend tests are conducted is of extreme importance, as some of our previous work has indicated. Applying a definite load in compression between parallel plates of a Baldwin-Southwark tensile test machine, as described under the paragraph entitled "Bend Tests," was found to give consistent, comparable results. It is conceivable that, where the same load was not applied or where care was not exercised in avoiding nicks or scratches at the sharp radius of the bend, erroneous results would be obtained.

Referring to Mr. E. P. Beachum's comments, it is believed that in determining the usefulness of any test, consideration must be given to the ultimate application and to the translation of the test results into the successful forming of parts. Our selection of the longitudinal rather than the transverse bend test was based entirely upon the greater severity of the longitudinal test rather than upon its utility.

The question of elimination of prior grain fragmentation by normalizing was considered insofar as it might affect the response to the bend test. Possibly the only accurate method of determining grain fragmentation would be by X-ray analysis. Such analysis was not applied in this investigation, but microscopic examination of the normalized samples showed uniform equiaxed crystals, indicating normal relief of strain, set up during cold rolling. Inasmuch as all of these samples were similarly handled in cold rolling and were produced to the same type of fine grain melting practice, the grain size and carbide distribution produced by the normalizing treatment were similar. It is believed that differences in prior treatment will affect the structure of the normalized steel, although in our investigation, care was taken to avoid such differences.

We would expect a rimming steel to act somewhat similarly to the low carbon steels, "T" and "U", in regard to grain growth. The spheroidization of the carbide is certainly not a problem in low carbon steels and, therefore, heavy reductions would not be required to aid spheroidization, but are necessary as a

control to obtain a fine recrystallized grain size. We would not anticipate any difficulty in obtaining flat longitudinal bends on rimming steels.

In answer to the last question concerning the bending quality of a conventional cold reduced box-annealed sheet, it should be pointed out that this type of product was not included in our present investigation. From the results obtained on steels "T" and "U", we would predict that no difficulty would be encountered in obtaining satisfactory longitudinal flat bends.

With the different finishing conditions postulated, differences in grain size and carbide condition would be anticipated, but such differences would be of insufficient magnitude to cause breaks during longitudinal flat bending.

THE Ar" RANGE IN SOME IRON-COBALT-TUNGSTEN ALLOYS

By W. P. SYKES

Abstract

In carbon-free alloys of iron, cobalt and tungsten the gamma to alpha transformation takes place throughout a range of temperature analogous to the Ar" range in steels.

For one ternary composition this range has been found to lie between 525 and 350 degrees Cent. (970 and 660 degrees Fahr.) approximately. The conclusions are based upon observations of microstructures and measurements of hardness.

By additions of chromium up to about 4 per cent the upper limit of the Ar" range is depressed to about 250 degrees Cent. (480 degrees Fahr.) while the lower limit appears to lie below the temperature of liquid air, -183 degrees Cent. (-300 degrees Fahr.).

The alpha phase which results from the transformation of gamma occurs in acicular form and the extent of the transformation appears to be governed solely by temperature and to be independent of time.

THE base composition of the alloys to be considered lies in the ternary section shown in Fig. 1. In the Ar' range (950 to 600 degrees Cent.) (1740 to 1110 degrees Fahr.) the product of gamma decomposition is distinctly lamellar as has been previously described (1).¹ Such a structure appears in Fig. 2.

From the nature of the constitutional diagram and the behavior of the alloys in cooling through the Ar' range, it seemed not unlikely that at lower temperatures the gamma to alpha transformation might proceed in a manner analogous to that observed in carbon steels.

It has been shown (2), moreover, that in an alloy of 50 per cent iron, 30 per cent cobalt and 20 per cent tungsten, quenched or air-cooled from the gamma range to 20 degrees Cent. (70 degrees Fahr.), the transformation of gamma is substantially complete. Upon subsequent heating to a temperature as low as 300 degrees Cent. (570

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. The author, W. P. Sykes, is metallurgical engineer, General Electric Co., Cleveland Wire Works, Cleveland. Manuscript received May 19, 1942.

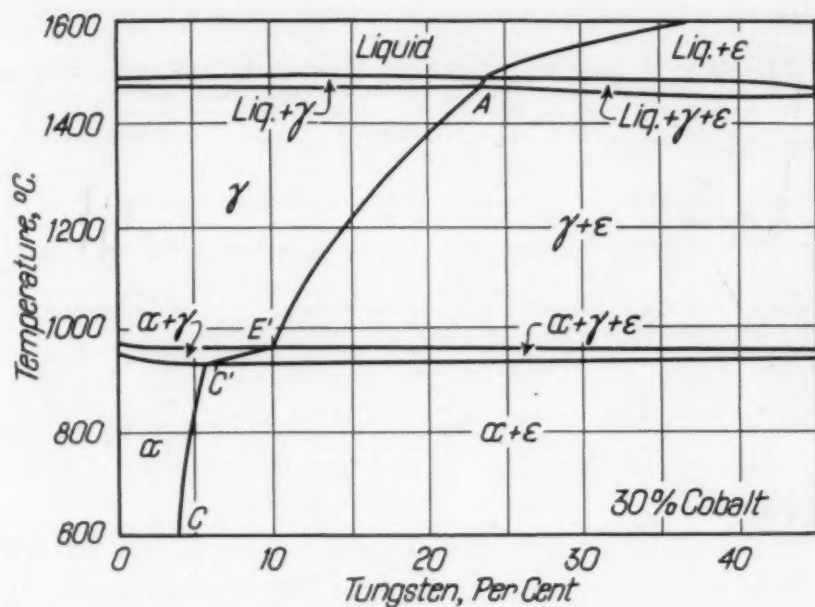


Fig. 1—Section Through Ternary System at 30 Per Cent Cobalt.

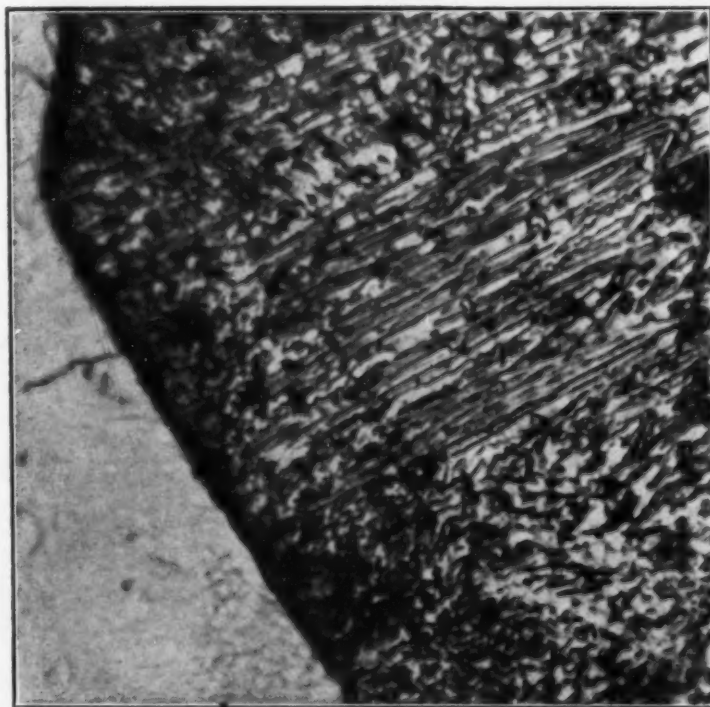


Fig. 2—Iron 70 Per Cent, Cobalt 20 Per Cent, Tungsten 10 Per Cent. Cooled from 1300 to 900 Degrees Cent. Over Period of 120 Hours. Lamellar Product of Gamma Decomposition in Ar' Range. $\times 1500$.

degrees Fahr.) precipitation hardening occurs, and with increasing rapidity as the temperature of the precipitation treatment is raised.

Table I
Rockwell C Hardness of Alloy No. 165, Solution Treated at 1350 Degrees Cent. Quenched in Lead at 550 Degrees Cent. Subsequent Treatments Described as "A" and "B"

Held at 550 Degrees Cent.	Treatment "A"	Treatment "B"
1 Hour	35-37	35-37
5 Hours	35-37	35-37
50 Hours	35-37	35-37

Treatment "A"—Water-Quenched from 550 to 20 degrees Cent. (1020 to 70 degrees Fahr.).
 Treatment "B"—Transferred directly from 550 degrees Cent. (1020 degrees Fahr.) to electric muffle at 600 degrees Cent. (1110 degrees Fahr.). Held at 600 degrees Cent. for 1 hour and water-quenched to 20 degrees Cent. (70 degrees Fahr.).

As shown in Fig. 3 the maximum hardness exhibited by this composition is attained in less than 1 hour at 600 degrees Cent. (1110 degrees Fahr.).

In binary alloys of iron and tungsten precipitation hardening is not observed at temperatures lower than 500 degrees Cent. (930 degrees Fahr.), and takes place quite slowly at 600 degrees Cent. (1110 degrees Fahr.). Such alloys, moreover, do not exhibit the gamma to alpha transformation, with the resulting grain refinement in the alpha solid solution. It would appear, then, that the latter structure is responsible for the enormously increased rate of precipitation hardening and by the same token a corresponding increase in the apparent diffusion rate of tungsten in alpha iron.

A simple experiment serves to demonstrate that an alloy of this type must be cooled to some minimum temperature before the characteristic rapid hardening will occur upon heating directly to 600 degrees Cent. (1110 degrees Fahr.) from this minimum temperature.

Such behavior is illustrated by the data in Table I. This alloy, when water-quenched or air-cooled from 1350 degrees Cent. (2460 degrees Fahr.) to room temperature, and then heated to 600 degrees Cent. (1110 degrees Fahr.), develops a maximum hardness of R_c 66 within a period of 1 hour.

As shown by the figures in Table I, no such hardening occurs if the alloy has been cooled to a minimum temperature of 550 degrees Cent. (1020 degrees Fahr.) before the treatment at 600 degrees Cent. (1110 degrees Fahr.). Such behavior implies that no alpha had been formed at 550 degrees Cent. (1020 degrees Fahr.) within which the rapid diffusion of tungsten can take place at 600 degrees Cent. (1110 degrees Fahr.). In other words, this temperature of 550 degrees Cent. (1020 degrees Fahr.) lies above the upper limit of a possible "Ar" range.

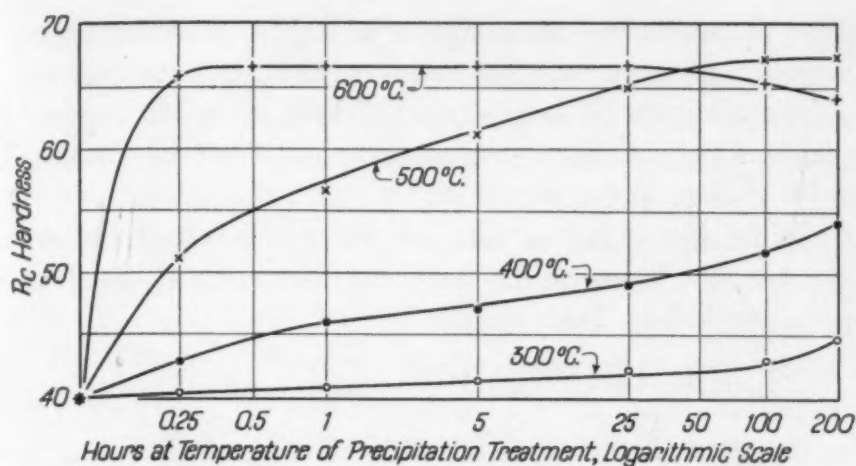


Fig. 3—Time-Hardness Curves for Ternary Alloy of Iron 50 Per Cent, Cobalt 30 Per Cent, Tungsten 20 Per Cent. Air-Cooled from 1350 Degrees Cent. and Aged at Temperatures Indicated.

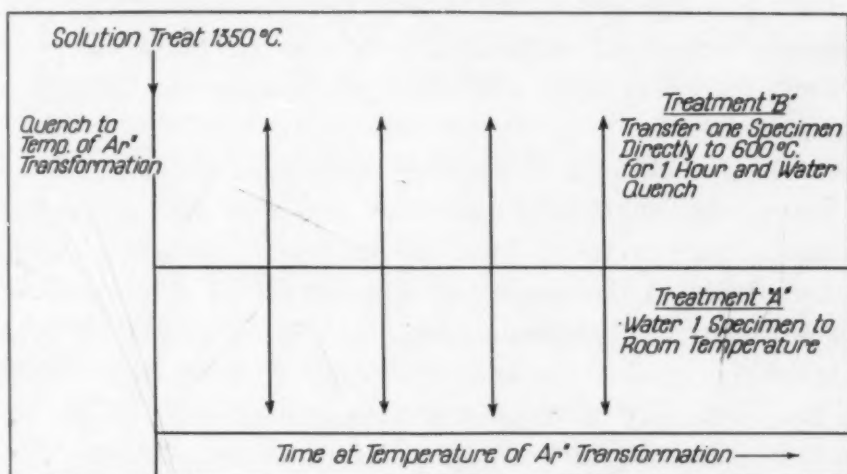


Fig. 3A—Chart Illustrating Treatments Employed.

Table II
Compositions of Alloys

Alloy No.	Cobalt Per Cent	Tungsten Per Cent	Chromium Per Cent	Iron
165	29.50	17.76	Balance
166	29.10	17.33	2.76	Balance
167	30.40	17.70	4.11	Balance

Silicon, 0.10 to 0.13 per cent
Manganese, 0.13 to 0.17 per cent
Carbon, 0.03 to 0.05 per cent

The diagram in Fig. 3A illustrates the sequence of treatments employed in this investigation. Descriptions of the microstructures and designations of the hardness curves in the following figures are given in terms of the treatments indicated in Fig. 3A.

From the microstructures shown in Fig. 4, it would appear that some diffusion and precipitation has occurred along the gamma grain boundaries during the 50-hour period of heating at 550 degrees Cent. (1020 degrees Fahr.). Such precipitation has, however, resulted in no measurable change in the overall hardness of this alloy.

In the following pages, data are presented which appear to fix approximately the limits of the Ar" range for each of the three compositions described in Table II.

COMPOSITIONS AND PREPARATION OF ALLOYS

To facilitate the interpretation of microstructures, the ternary composition, No. 165, was selected. This furnishes a single phase structure after solution treatment at 1350 degrees Cent. (2460 degrees Fahr.). The chromium-bearing modifications, Nos. 166 and 167, likewise composed substantially of a single phase, were chosen to illustrate the effect of an additional solute upon the location of the Ar" range.

Details of melting and working have been described elsewhere (2). Specimens for thermal treatment, about $\frac{3}{8}$ inch in length, were cut from swaged rods $\frac{1}{2}$ inch in diameter. Solution treatments were carried out in the hydrogen atmosphere of a tungsten wound resistor furnace. A 30-minute period seemed to suffice for complete solution of the epsilon phase in the case of alloy 165. A longer period was necessary to approach complete solution in the case of the chromium-bearing alloys. In order to avoid excessive variation in grain size, therefore, all solution treatments were extended to periods of 1 hour.

Molten lead and low melting alloys served as quenching media for the temperatures between 550 and 175 degrees Cent. (1020 and 350 degrees Fahr.).

Unless otherwise specified all microsections were etched for 5 seconds in a mixture composed of four parts hydrogen peroxide and one part phosphoric acid. The alpha phase, after the precipitation treatment at 600 degrees Cent. (1110 degrees Fahr.), is rapidly darkened by this etchant. Unless precipitation has occurred within the alpha, however, it is less readily attacked.

THE Ar" RANGE IN ALLOY No. 165

Alpha in acicular form was observed first in this composition

when quenched from 1350 to 525 degrees Cent. (2460 to 980 degrees Fahr.), held for 15 minutes at this temperature, then transferred in heated tongs to an adjacent muffle at 600 degrees Cent. (1110 degrees Fahr.) and after 1 hour water quenched. The resulting microstructure appears in Fig. 5.

The darkly etched clusters of acicular figures presumably represent the alpha solid solution formed from gamma at 525 degrees Cent. (980 degrees Fahr.) and within which precipitation of the tungsten-rich phase (epsilon) has taken place during subsequent heating at 600 degrees Cent. (1110 degrees Fahr.). The lighter matrix marks that portion of the structure which was still unaltered gamma at the end of the 600 degrees Cent. (1110 degrees Fahr.) treatment, but which subsequently transformed to alpha during the quench to room temperature.

In a companion specimen, quenched directly to room temperature after 15 minutes at 525 degrees Cent. (980 degrees Fahr.), the darkening of the alpha by an identical etch is but moderate as may be seen in Fig. 6. In this case susceptibility to the etchant is the result of limited precipitation within alpha during the 15-minute period at 525 degrees Cent. (980 degrees Fahr.).

The technique of identifying the alpha phase by direct transfer from the quenching bath to a higher temperature, resulting in rapid precipitation, has been described by Greninger and Troiano (3). These investigators employed a tempering bath held at 275 degrees Cent. (530 degrees Fahr.) to bring about etch darkening within the needles of martensite after quenching plain carbon steels to some lower temperature within the Ar³ range.

If the time of holding at 525 degrees Cent. (980 degrees Fahr.) is extended to 100 hours, the resulting structure appears as shown in Fig. 7. Obviously there has been no increase in the quantity of alpha present as compared to that seen after the 15-minute period at 525 degrees Cent. (980 degrees Fahr.). Precipitation seems to have progressed at the boundaries of the gamma grains as evidenced by the "fuzzy" appearance marking these regions.

Upon lowering the temperature of the quenching bath to 500 degrees Cent. (930 degrees Fahr.) the structures resulting from holding periods of 15 minutes and 100 hours are illustrated in Figs. 8 and 9 respectively. The quantity of alpha has been considerably increased, but again time at the temperature of quench has produced no measurable effect upon the amount of acicular alpha.

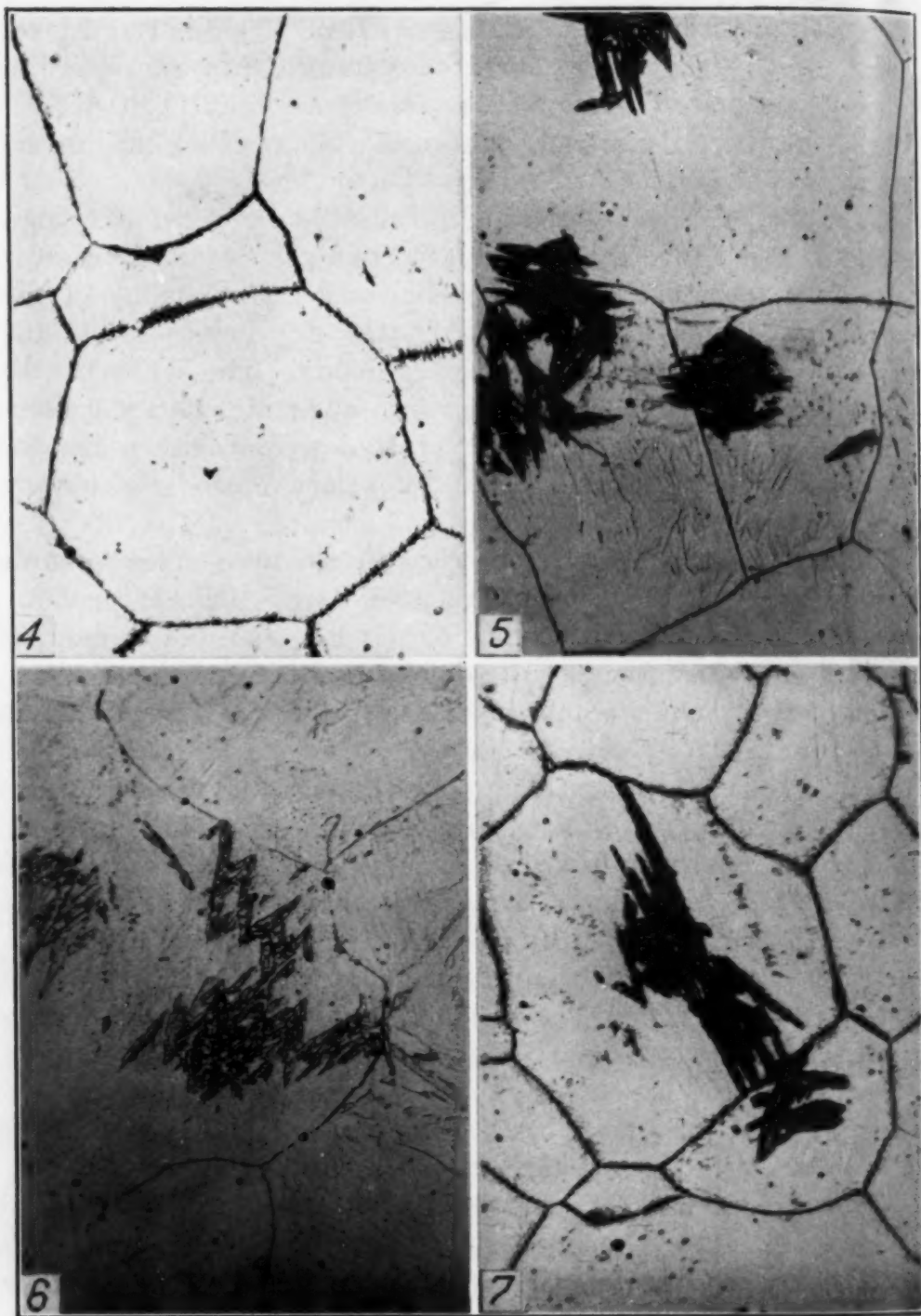


Fig. 4—Alloy No. 165. Quenched from 1350 to 550 Degrees Cent. Held at 550 Degrees Cent. for 50 Hours. Water-Quenched. $\times 200$.

Fig. 5—Alloy No. 165. Quenched from 1350 to 525 Degrees Cent. Held for 15 Minutes. Treatment "B". $\times 200$.

Fig. 6—Alloy No. 165. 525 Degrees Cent. for 15 Minutes. Treatment "A". $\times 200$.

Fig. 7—Alloy No. 165. 525 Degrees Cent. for 100 Hours. Treatment "B". $\times 200$.



- Fig. 8—Alloy No. 165. 500 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.
Fig. 9—Alloy No. 165. 500 Degrees Cent. for 100 Hours. Treatment "B".
× 200.
Fig. 10—Alloy No. 165. 475 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.
Fig. 11—Alloy No. 165. 450 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.

Fields were selected for photomicrographs which seemed to be representative as nearly as possible. Some local nonuniformities existed in all the specimens, however, so that by intentional choice the effect of time might have been shown to either increase or decrease the quantity of alpha.

Quenching to still lower temperatures resulted in the structures appearing in Figs. 10 and 11. The almost complete darkening observed after quenching to 450 degrees Cent. (840 degrees Fahr.) and transferring to 600 degrees Cent. (1110 degrees Fahr.) for 1 hour might be taken to indicate total transformation of gamma at this temperature. As will be shown presently, however, the hardness developed by the treatment at 600 degrees Cent. (1110 degrees Fahr.) is in this case only R_c 63 as compared with the possible maximum R_c 66, which results from cooling this alloy to 20 degrees Cent. (70 degrees Fahr.) prior to the precipitation treatment at 600 degrees Cent. (1110 degrees Fahr.).

HARDNESS CHANGES ACCOMPANYING TREATMENTS DESCRIBED ABOVE

As may be seen from the time-hardness curves of Fig. 3, appreciable precipitation hardening occurs within the alpha phase at temperatures as low as 400 degrees Cent. (750 degrees Fahr.). Hence in an alloy quenched to 500 degrees Cent. (930 degrees Fahr.) the hardness might be expected to increase moderately as the holding time at this temperature is prolonged. This hardness change was detected by Rockwell measurements made upon specimens subjected to treatment "A" as outlined in Fig. 3-A. It is attributed to precipitation within the alpha formed when the alloy reached the temperature of the quenching medium. Such hardening should proceed at a rate normal for the holding temperature, and should reach a maximum value determined by the amount of alpha present and also by the time of holding.

As extreme results of treatment "B" the hardness should be expected (a) to remain unchanged in case no gamma has transformed to alpha at the temperature of the quenching medium, or (b) to reach the maximum developed by the alloy in case such transformation has been complete.

The absence of any hardness change after either treatment "A" or "B" is demonstrated by the data in Table I.

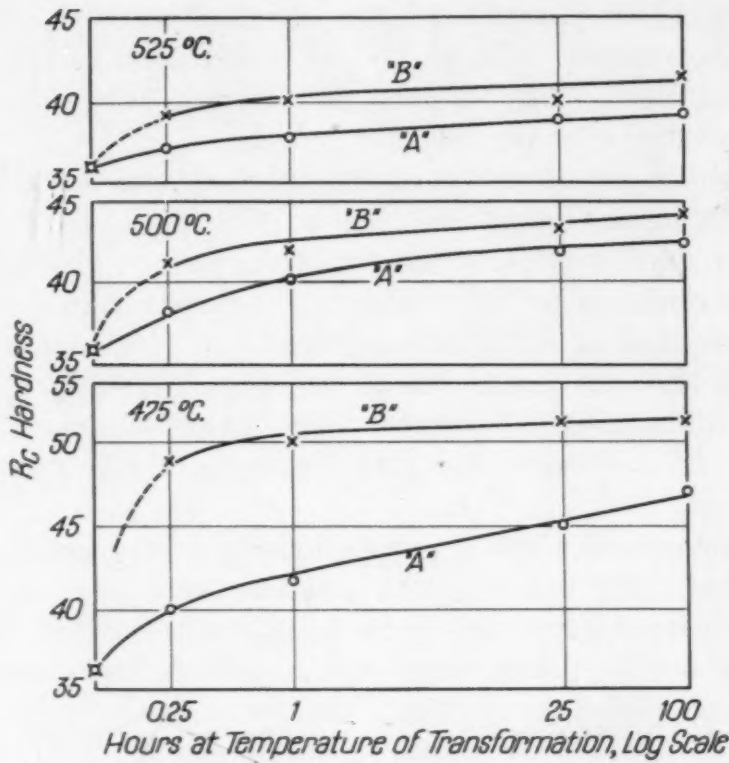


Fig. 12—Time-Hardness Curves from Treatments "A" and "B". Alloy No. 165. Quenched to 525, 500 and 475 Degrees Cent.

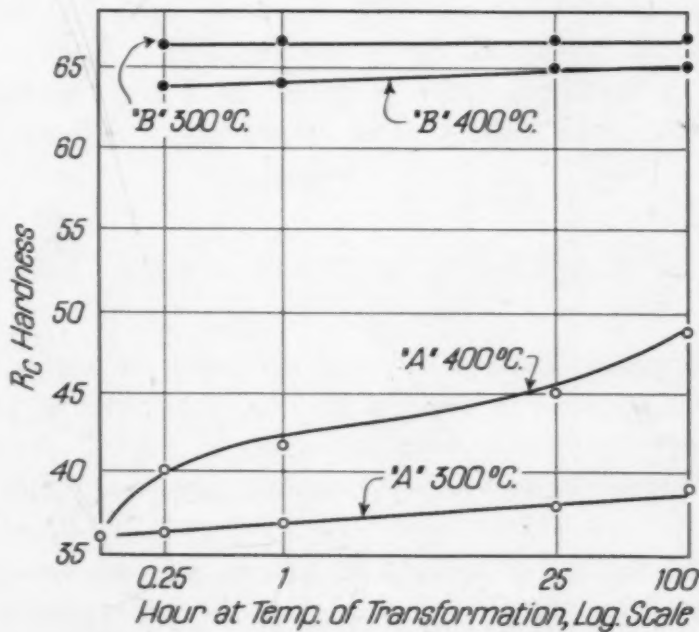


Fig. 13—Time-Hardness Curves from Treatments "A" and "B". Alloy No. 165. Quenched to 400 and 300 Degrees Cent.

In Fig. 12 are plotted the hardness values observed in alloy No. 165 after treatments "A" and "B" when quenched to 525, 500 and 475 degrees Cent. (980, 930 and 885 degrees Fahr.) and held at these temperatures for the indicated periods.

A comparison of the hardening performance at 525 degrees Cent. (980 degrees Fahr.) with that at 475 degrees Cent. (885 degrees Fahr.) will serve to demonstrate the factors which determine the final hardness of the alloy subjected to these treatments. As the result of treatment "A" at 525 degrees Cent. (980 degrees Fahr.) the overall hardness has increased but slightly. Opportunity for further hardening at 600 degrees Cent. (1110 degrees Fahr.) by treatment "B" is likewise restricted due to the meager proportion of alpha present.

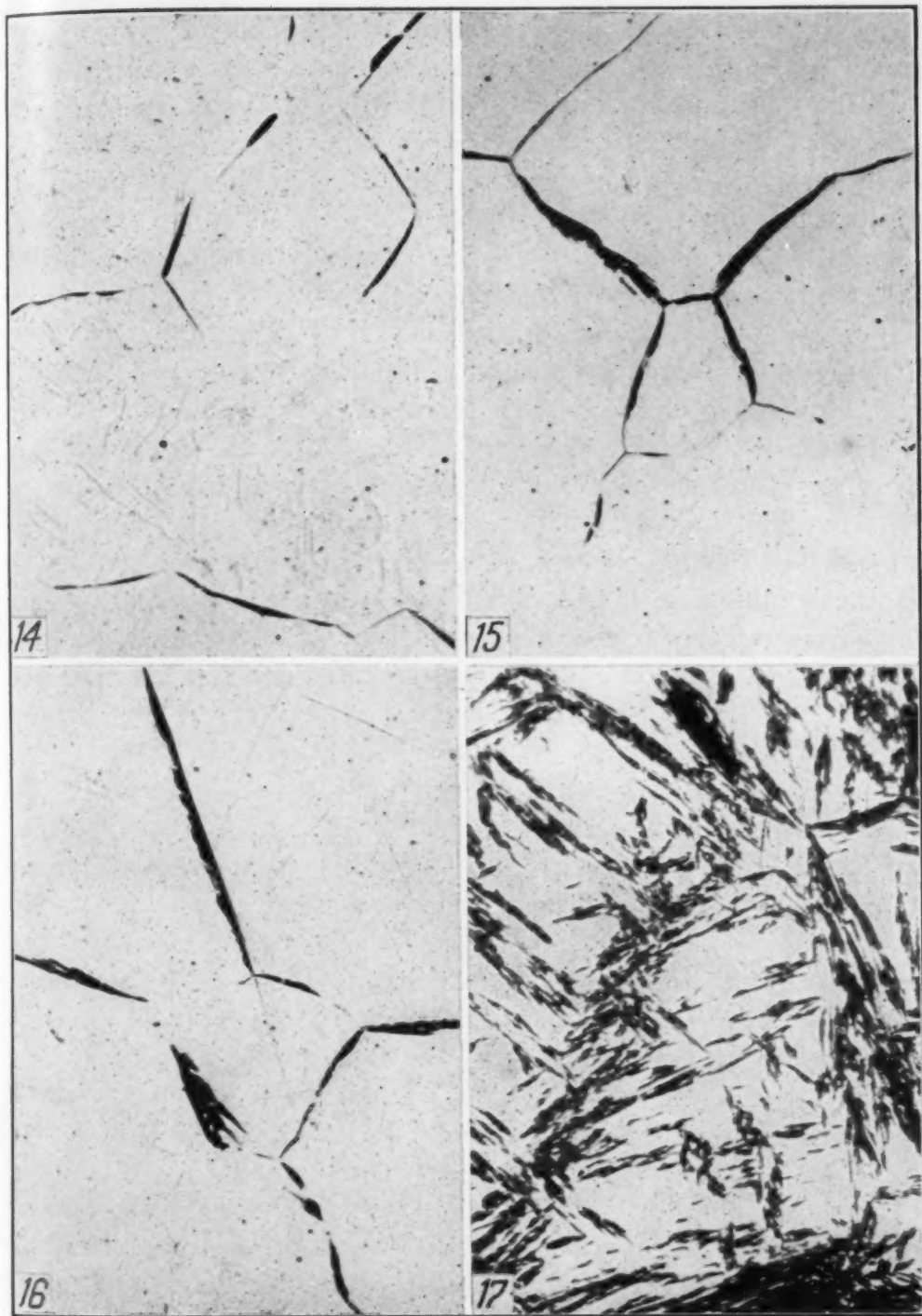
The amount of alpha is greatly increased by quenching to 475 degrees Cent. (885 degrees Fahr.), as has been shown in Fig. 10. This circumstance is reflected by the hardness data of Fig. 12. Even though the rate of precipitation within alpha is lower than at 525 degrees Cent. (980 degrees Fahr.), the overall hardening from treatment "A" is considerably enhanced. More striking, perhaps, is the marked rise in hardness brought about by treatment "B".

From the data shown in Fig. 13 it would seem that the gamma transformation was complete at some temperature between 400 and 300 degrees Cent. (750 and 570 degrees Fahr.) on the basis of hardness values observed after treatment "B". The alloy attains its maximum hardness within a period of 1 hour at 600 degrees Cent. (1110 degrees Fahr.) after quenching to 300 degrees Cent. (570 degrees Fahr.).

THE A_r RANGE IN ALLOYS MODIFIED WITH CHROMIUM

The foregoing data show that diffusion of tungsten occurs within the alpha phase throughout the A_r range of the alloy under consideration. In fact the microstructures in Figs. 7 and 9 suggest that at the higher temperatures diffusion may take place slowly in gamma.

No small amount of speculation has, in the past, centered about the part played by diffusion in producing the microstructures which result from isothermal decomposition of gamma in the A_r range. Most of this discussion has concerned iron-carbon alloys in which



- Fig. 14—Alloy No. 166. 350 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.
Fig. 15—Alloy No. 166. 325 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.
Fig. 16—Alloy No. 166. 325 Degrees Cent. for 100 Hours. Treatment "B".
× 200.
Fig. 17—Alloy No. 166. 250 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.

the diffusion rate of carbon in ferrite is appreciable at temperatures as low as 20 degrees Cent. (70 degrees Fahr.).

In order to observe structures formed by the gamma-alpha transformation at temperatures so low as to eliminate the element of diffusion, two alloys were prepared, numbers 166 and 167, the composition of which are listed in Table II.

Alloy 166 first shows the presence of alpha after treatment "B" when quenched to 350 degrees Cent. (660 degrees Fahr.), and the resulting structure appears in Fig. 14. It is apparent that alpha is first formed along the boundaries of the gamma grains.

At 325 degrees Cent. (615 degrees Fahr.) the amount of alpha is seen to be increasing as shown in Fig. 15, but is still confined to the grain boundary location. Fig. 16 represents the structure after 100 hours at 325 degrees Cent. (615 degrees Fahr.), which reveals no change as compared to that in Fig. 15, which was held for 15 minutes at the same temperature. Again in Figs. 17 and 18 appear the microstructures of the alloy quenched to 250 degrees Cent. (480 degrees Fahr.) and held for 15 minutes and for 100 hours respectively. As the transformation temperature is successively lowered through 225, 175 and 100 degrees Cent. (435, 350 and 210 degrees Fahr.) the amount of alpha formed increases as indicated by the darkly etched portions and is shown in Figs. 19, 20 and 21. The quench in boiling water appears to have resulted in a complete transformation of gamma, as indicated both by the etching characteristics (Fig. 21) and by the resulting hardness of R_c 67. Immersion in liquid air is not effective in raising this hardness which is developed by subsequent heating at 600 degrees Cent. (1110 degrees Fahr.).

In the case of alloy 167 the upper limit of the A_r'' range appears to lie near 250 degrees Cent. (480 degrees Fahr.), since after quenching to that temperature traces of alpha are found as shown in Fig. 22. Considerable gamma remains in this composition after cooling to 100 degrees Cent. (210 degrees Fahr.). This is indicated by the unetched areas in the microstructure of Fig. 23. Evidence of retained gamma after cooling to room temperature is seen likewise in the microstructure shown in Fig. 24 at 1000 diameters.

This gamma is largely transformed by immersing the alloy in liquid air. The resulting structure to be seen in Fig. 25 still contains sufficient gamma to furnish very weak reflections in the X-Ray diffraction pattern as compared with the stronger reflections fur-

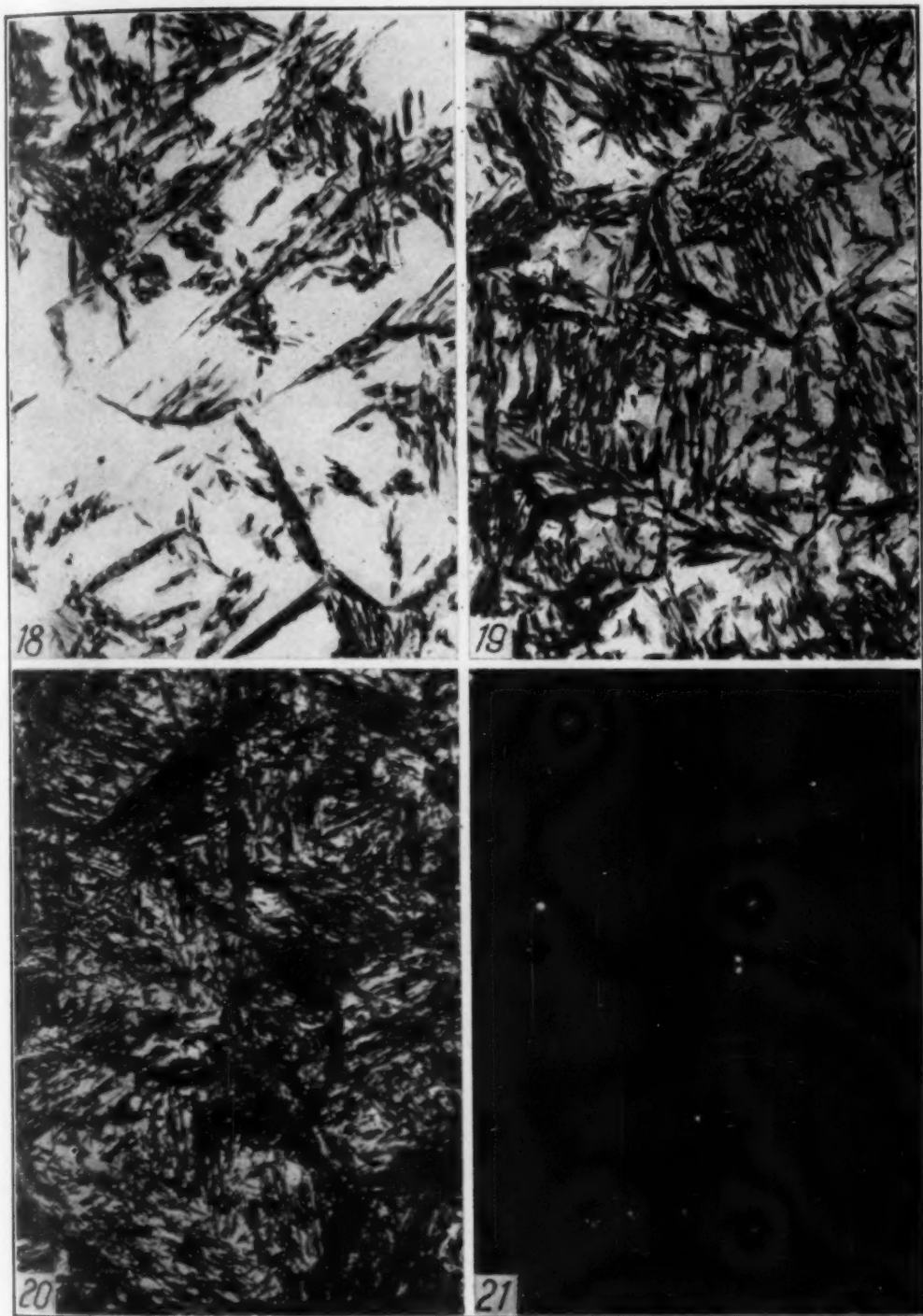


Fig. 18—Alloy No. 166. 250 Degrees Cent. for 100 Hours. Treatment "B".
× 200.

Fig. 19—Alloy No. 166. 225 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.

Fig. 20—Alloy No. 166. 175 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.

Fig. 21—Alloy No. 166. 100 Degrees Cent. for 15 Minutes. Treatment "B".
× 500.

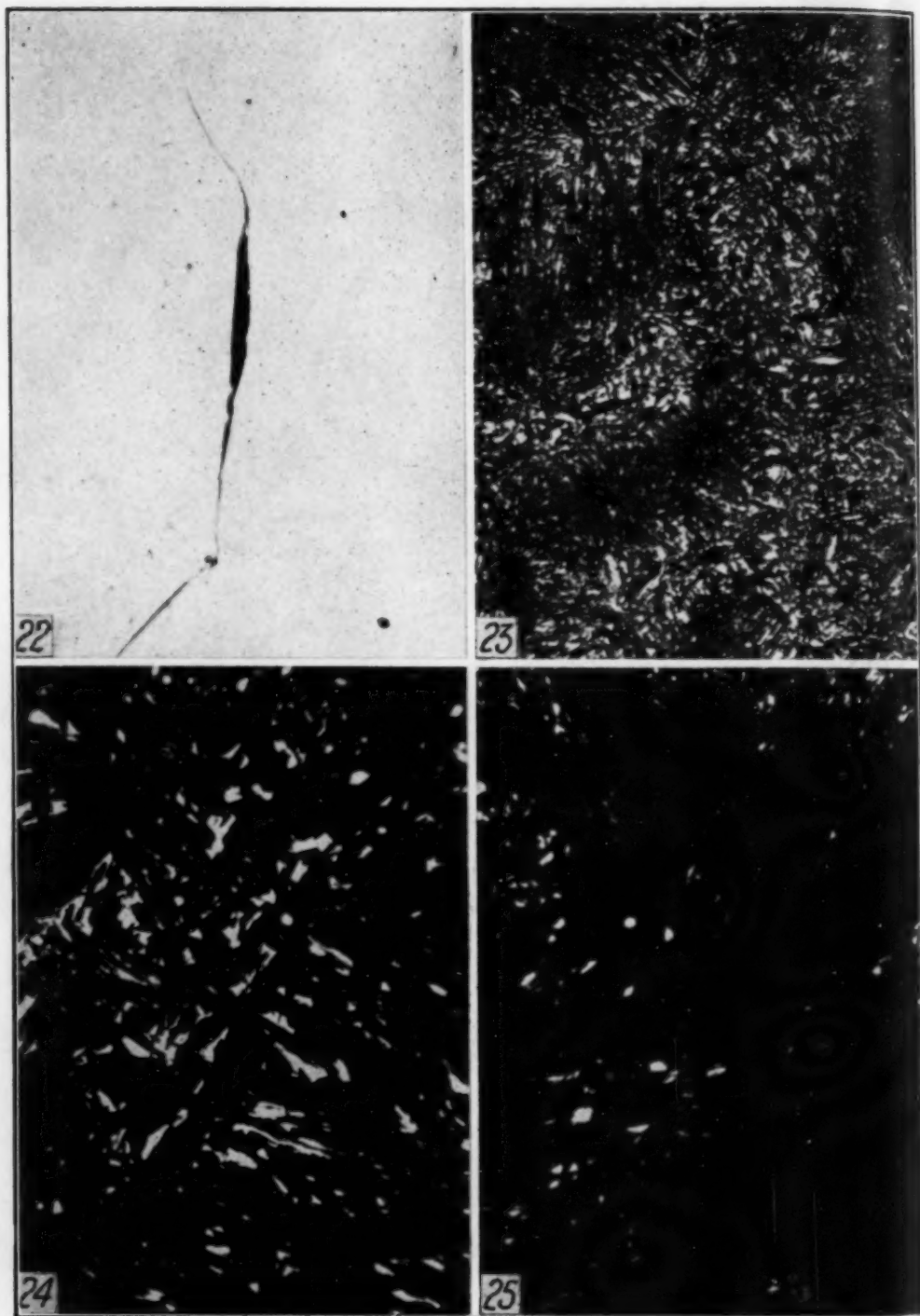


Fig. 22—Alloy No. 167. 250 Degrees Cent. for 15 Minutes. Treatment "B".
× 500.

Fig. 23—Alloy No. 167. 100 Degrees Cent. for 15 Minutes. Treatment "B".
× 200.

Fig. 24—Alloy No. 167. Quenched to 20 Degrees Cent. Treatment "B". × 1000.

Fig. 25—Alloy No. 167. Immersed in Liquid Air Before Aging at 600 Degrees Cent. × 1000.

nished by the alloy when cooled only to 20 degrees Cent. (70 degrees Fahr.). Some of the rounded white spots in Figs. 24 and 25 very probably represent a residue of the tungsten-rich phase carried over from the solution treatment.

To approximate the lower limit of the Ar'' range for this alloy, it was cooled to a temperature of -50 degrees Cent. (-60 degrees Fahr.). Upon subsequent aging at 600 degrees Cent. (1110 degrees Fahr.) it developed a hardness of R_c 68, equal to that shown by a specimen cooled to -183 degrees Cent. (-300 degrees Fahr.) and the microstructures were substantially identical. This hardness exceeds by two points that shown by the alloy cooled only to 20 degrees Cent. (70 degrees Fahr.) and suggests that in this composition some gamma will remain untransformed even at -183 degrees Cent. (-300 degrees Fahr.).

HARDNESS CHANGES OBSERVED IN TREATMENTS OF ALLOYS 166 AND 167

Since the Ar'' ranges for these alloys lie below 350 degrees Cent.

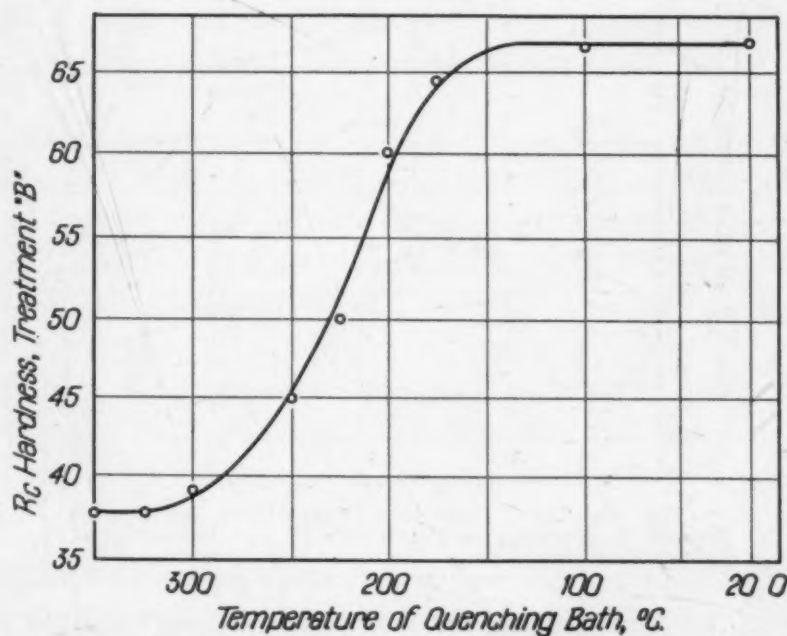


Fig. 26—Chart Illustrating Transformation Temperature Versus Final Hardness by Treatment "B". Alloy No. 166.

(660 degrees Fahr.) no measurable hardening occurred during the periods of holding at temperature subsequent to quenching.

Upon transferring to 600 degrees Cent. (1110 degrees Fahr.)

by schedule "B", however, the magnitudes of the resulting hardness values were in satisfactory agreement with the observed microstructures except at the extremes of the ranges.

In Fig. 26, for example, are plotted the hardness values obtained by treatment "B" from a series of quenching temperatures covering the Ar" range of alloy No. 166.

While the microstructure showed the upper limit of this range to approximate 350 degrees Cent. (660 degrees Fahr.) the quantity of alpha formed was insufficient to cause a measurable increase in hardness upon aging at 600 degrees Cent. (1110 degrees Fahr.). Such an increase was first noticeable after quenching to 300 degrees Cent. (570 degrees Fahr.).

DISCUSSION

From the data furnished by microstructures and hardness measurements it is possible to construct the chart shown in Fig. 27.

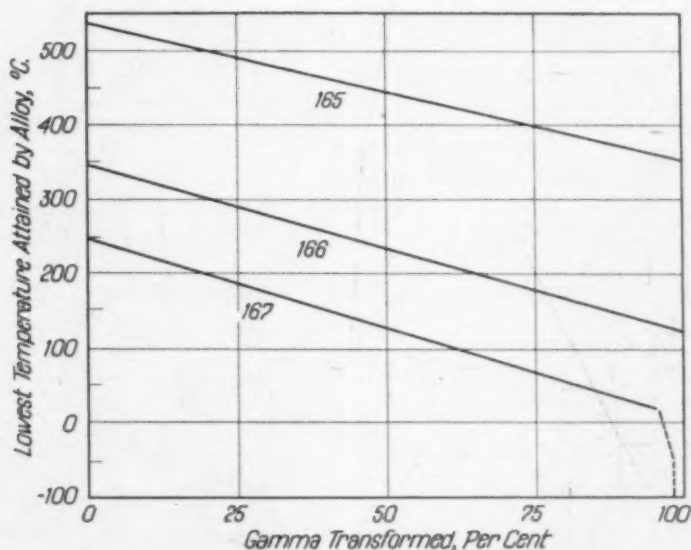


Fig. 27—Chart Illustrating Approximate Relationship Between Temperature of Transformation and Percentage of Gamma Transformed.

This serves to approximate the extent of the Ar" ranges for the three alloys investigated. It is admittedly not quantitative and is especially questionable as regards the lower limits of these ranges which were fixed principally from hardness data.

Since the co-ordinates in this diagram are (a) temperature of transformation and (b) quantity of gamma transformed, it is strik-

ingly similar to the one proposed by Troiano (3) to represent the extent of martensite formation as a function of temperature.

Greninger and Troiano (3) have reported the lowering of the Ar'' range which results from increasing the carbon content in plain carbon steels from 0.7 to 1.8 per cent. This relationship has also been observed by Digges (4). That a like effect is produced by chromium as a solute in the alloys under consideration here may be deduced from the chart of Fig. 27.

The omission of microstructures in this paper representative of holding periods shorter than 15 minutes will very likely raise the question as to changes in structure which might have occurred over still shorter periods. That is of course a pertinent query. In explanation it may be stated that no structural differences were observed between specimens held for 5 minutes and those held for 15 minutes at the temperature of the quenching medium. Some irregularities did appear when the holding time was less than about 5 minutes. One reason for this is undoubtedly the relatively large size of specimen and the lack of data to determine the time required for the specimen to come to temperature. On the other hand, the size of the specimen minimized the danger of cooling during transfer from the quenching bath to the muffle at 600 degrees Cent. (1110 degrees Fahr.).

No discussion will be offered at this time regarding the Ar' ranges of these alloys. It seems pertinent to mention, however, that the critical cooling rates through these ranges are surprisingly low. In fact specimens of the size employed may be cooled from 1350 degrees Cent. (2460 degrees Fahr.) in air to a dull red, placed in a muffle at a temperature within the Ar' range and will yield microstructures and hardness values which appear to be identical with those found in specimens quenched to the same temperature.

SUMMARY

Based upon the data furnished by microstructures and hardness measurements, the Ar'' range for a ternary alloy of iron 53 per cent, cobalt 30 per cent and tungsten 17 per cent has been determined. This extends from about 525 degrees Cent. (980 degrees Fahr.) to about 350 degrees Cent. (660 degrees Fahr.).

For similar alloys modified by additions of 2.7 and 4.1 per cent chromium the Ar'' ranges are considerably depressed.

Over the interval extending from 5 minutes to 100 hours the transformation of gamma to alpha appears to be independent of the time factor.

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DISCUSSION

Written Discussion: By Alden B. Greninger, General Electric Company Lamp Department, Cleveland.

Dr. Sykes has here given us additional information on heat treatments of his very interesting series of iron-cobalt-tungsten alloys. Evidently the extreme hardnesses of 67 Rockwell C developed by these carbon-free alloys are a consequence of two reactions: (1) the formation of martensite from the austenite solid solution on cooling, and (2) the subsequent high temperature age hardening of the martensite structure, whereby the specimen hardness increases from about 35 to 67 Rockwell C. Any retained austenite remains unaffected by the age-hardening treatment that produces such extreme change in the hardness of the martensite.

Thus, Dr. Sykes has added another alloy to the rapidly growing list of alloys showing the martensite transformation. Except for age hardening, the similarity between the behaviors of these alloys and those of iron-carbon alloys is striking. Incidentally, the effect of chromium in lowering A_r when added to these ternary carbon-free alloys (shown in Fig. 27) is similar to its effect when added to iron-carbon alloys; that is, for a given carbon content, A_r is lowered as chromium content increases.

Oral Discussion

M. A. GROSSMANN:² In the short time that Dr. Sykes had for his presentation, he did not touch on one point that seems particularly interesting and significant; it bears on the highly debated question of the kinetics of transformation in steels from austenite to martensite. Particularly interesting it seems to me was the last slide, showing the change effected by small amounts of chromium in this highly complex alloy, a change in the temperature at which the transformation takes place, as induced by changes in the chromium.

²Director of research, Carnegie-Illinois Steel Corp., Chicago.

I wonder if Dr. Sykes would care to discuss that point a little, in relation to the work of Greninger and Troiano, as there seems to be a marked analogy here.

Author's Reply

The experimental evidence presented in this paper surely indicates that the austenite to martensite transformation as observed in these alloys has much in common with that transformation in the steels. I do not feel competent to discuss the subject from the standpoint of kinetics, but hope in the future to investigate more completely the A_r' reactions in these materials. From the evidence now at hand it would appear that the austenite decomposition in the A_r' range is likewise strikingly analogous to the corresponding decomposition as observed in steels.

CORROSION OF WATER PIPES IN A STEEL MILL

BY C. L. CLARK AND W. J. NUNGESTER

Abstract

This paper presents the results of an investigation undertaken to determine the cause of severe corrosion in the cooling water lines of a steel mill. Chemical analysis of the corrosion products showed both sulphides and free sulphur. Since neither of these were present in the original well water, the action of sulphate-reducing bacteria was indicated. Considerable circumstantial evidence was obtained to indicate that these bacteria were the cause of the attack.

A bacteriological investigation was made to substantiate the above findings. Examination of the water and of the corrosion products definitely showed these bacteria to be present. Likewise laboratory experiments were able to reproduce, in a few weeks time, the formation of iron sulphide.

INTRODUCTION

CONSIDERABLE attention has long been given to the general subject of corrosion of ferrous materials but the annual losses due to this cause still are enormous. Because of the present-day scarcity of steel the prevention of corrosion is of even greater importance, for every pound of metal conserved is a pound of melting capacity saved.

For the past 3 years corrosion, in varying degrees, has been occurring in the water cooling lines of the Steel Plant of The Timken Roller Bearing Company. At first this corrosion was rather slight but recently it has become much more severe, certain of the lines having a life of only a few months. This problem is very serious to a steel mill, for a complete failure of the cooling system would not only cause an interruption in production but would damage the equipment, especially the electric melting furnaces and their auxiliary apparatus.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. Of the authors, C. L. Clark is research metallurgical engineer, Timken Roller Bearing Co., Canton, Ohio, and W. J. Nungester is associate professor of bacteriology, University of Michigan, Ann Arbor, Mich. Manuscript received June 22, 1942.

The cause of this corrosion was traced to sulphur bacteria. This form of attack has been known for over 100 years but it is not believed to be generally recognized, and it is, therefore, entirely possible that corrosion of this type has been confused with other forms. Since a proper analysis of the cause of attack will greatly hasten its elimination and thus conserve metals, it was believed advisable to describe the particular conditions encountered.

SOURCE AND ANALYSIS OF WATER

The water used for cooling purposes is obtained from a well which is approximately 150 feet deep by 12 feet in diameter. At the base of the well thirty-six pipes, 8-inch diameter, extend radially outwards for feeding. Five pumps draw the water from a zone 8 feet from the bottom of the well. The capacity is 30 million gallons per day. The temperature of the water as it leaves the well is 52 degrees Fahr. (10 degrees Cent.) and the pH varies from 6.7 to 7.8.

The analysis of water samples taken at the well, and after it had served for cooling the No. 8 electric melting furnace and the heating furnace for the 10-inch mill, is given in Table I. The analyses at these three points are nearly identical, and yet little if any corrosion has occurred at the 10-inch mill furnace, while it has been severe at the No. 8 furnace and in the enclosed metal parts of the well.

On the basis of these analyses this water would not appear to be corrosive, at least to the extent encountered. The problem was further complicated by the fact that the city water of Canton was of approximately the same analysis and yet no marked corrosion occurred in any of the city water lines.

Table I
Analysis of Water Samples from Designated Points in the Mill

	Well	At No. 8 Furnace	At Furnace of 10" Mill
Odor	None	Slight	None
Color	None	None	None
Turbidity	Clear	Clear	Clear
Chlorine (Chloride)	24.7 ppm	24.7 ppm	24.7 ppm
SO ₂	146. ppm	143. ppm	144. ppm
SiO ₂	12. ppm	12. ppm	12.5 ppm
R ₂ O ₃	4. ppm	4. ppm	4.5 ppm
CaO	197. ppm	199. ppm	195. ppm
MgO	50.9 ppm	50.2 ppm	50.9 ppm
Total Residue	615. ppm	625. ppm	640. ppm
Ignition Loss	75. ppm	70. ppm	130. ppm
Alkalinity (CaCO ₃)	292. ppm	292. ppm	292. ppm

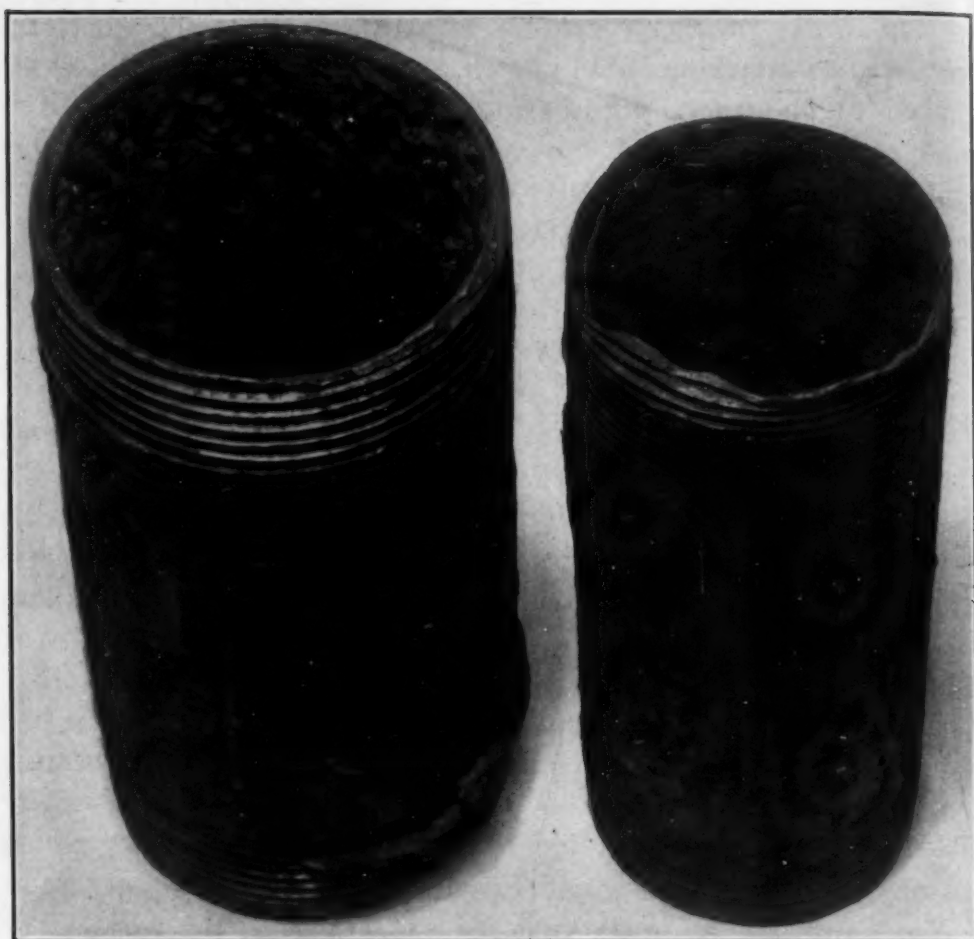


Fig. 1—Photograph Showing Two Different Types of Attack on the Inner Wall of Water Pipe.

CORROSION CHARACTERISTICS

Representative examples of corroded pipe sections are shown in Figs. 1 to 4. The corrosion may be classified as of two types. In one the attack is general, the entire pipe wall being reduced in section; while in the other tube attack is selective, leaving small islands of the original metal remaining. These two conditions are illustrated in Fig. 1.

The pipe lines throughout the mill are not buried and all of the corrosion occurs on the inner wall. Fig. 2 shows sliced sections of pipes in which, at the threaded ends, the walls are completely corroded through. The wall thickness throughout the entire section has, however, been considerably reduced.

Fig. 3 is a sliced section of a fitting removed from one of the lines. The inner portion of the wall is seen to be of a darker color

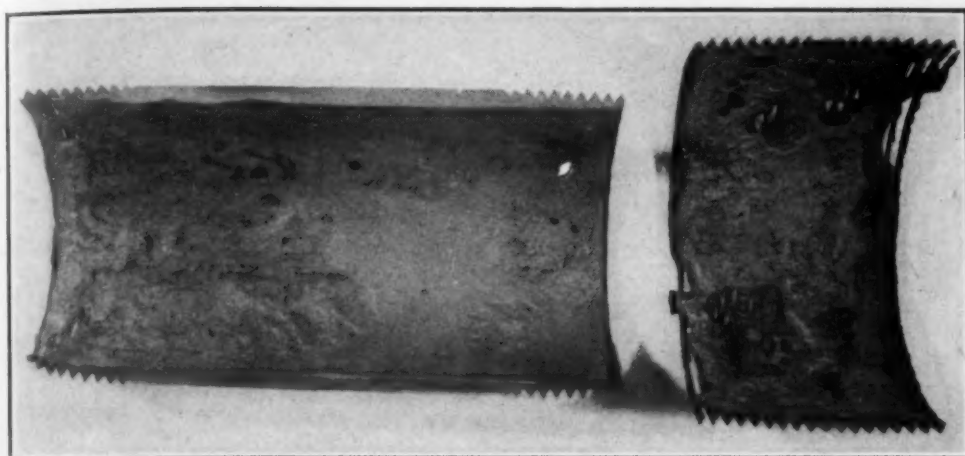


Fig. 2—Etched Sliced Sections Showing Severity of Attack.

than the remainder. This darker material is relatively soft and can be readily cut with a pocket-knife.

The severity of attack in a pipe section adjacent to a welded flange is shown in Fig. 4. In general the corrosion appeared to be worse in those sections where turbulence was liable to occur.

The dried corrosion products were removed from pipe sections, such as shown in Fig. 1, and from the fitting of Fig. 3, and subjected to chemical analyses with the following results:

Specimen Number	Cl	SO ₃	R ₂ O ₃	Sulphur, Free or as Sulphide	SiO ₂	CaO	MgO	Ignition Loss
A	Nil	Nil	48.6	23.90	6.60	Nil	Nil	19.51
B	Nil	Nil	51.3	11.62	0.70	15.0	.05	21.33
C	Nil	Nil	52.40	3.71	19.04	Nil	Nil	24.85

A: Outer layer of corroded products from pipes of Fig. 1.

B: Inner layer of corroded products from pipes of Fig. 1.

C: Dark deposit removed from inner surface of fitting of Fig. 3.

The outstanding fact in these analyses is the presence of large amounts of free sulphur even though the well water showed very little if any of this element to be present. It is true that the water did contain sulphates but under the given operating conditions, there is no chemical reaction by which sulphates can be reduced to free sulphur. This raised the question as to whether or not the so-called "sulphur bug" might not be present and the cause of the major portion of the attack.

REVIEW OF THE LITERATURE

Knowledge of sulphur bacteria, that is, bacteria which reduces SO_4^- to S^- and finally free sulphur, extends back to the last century.

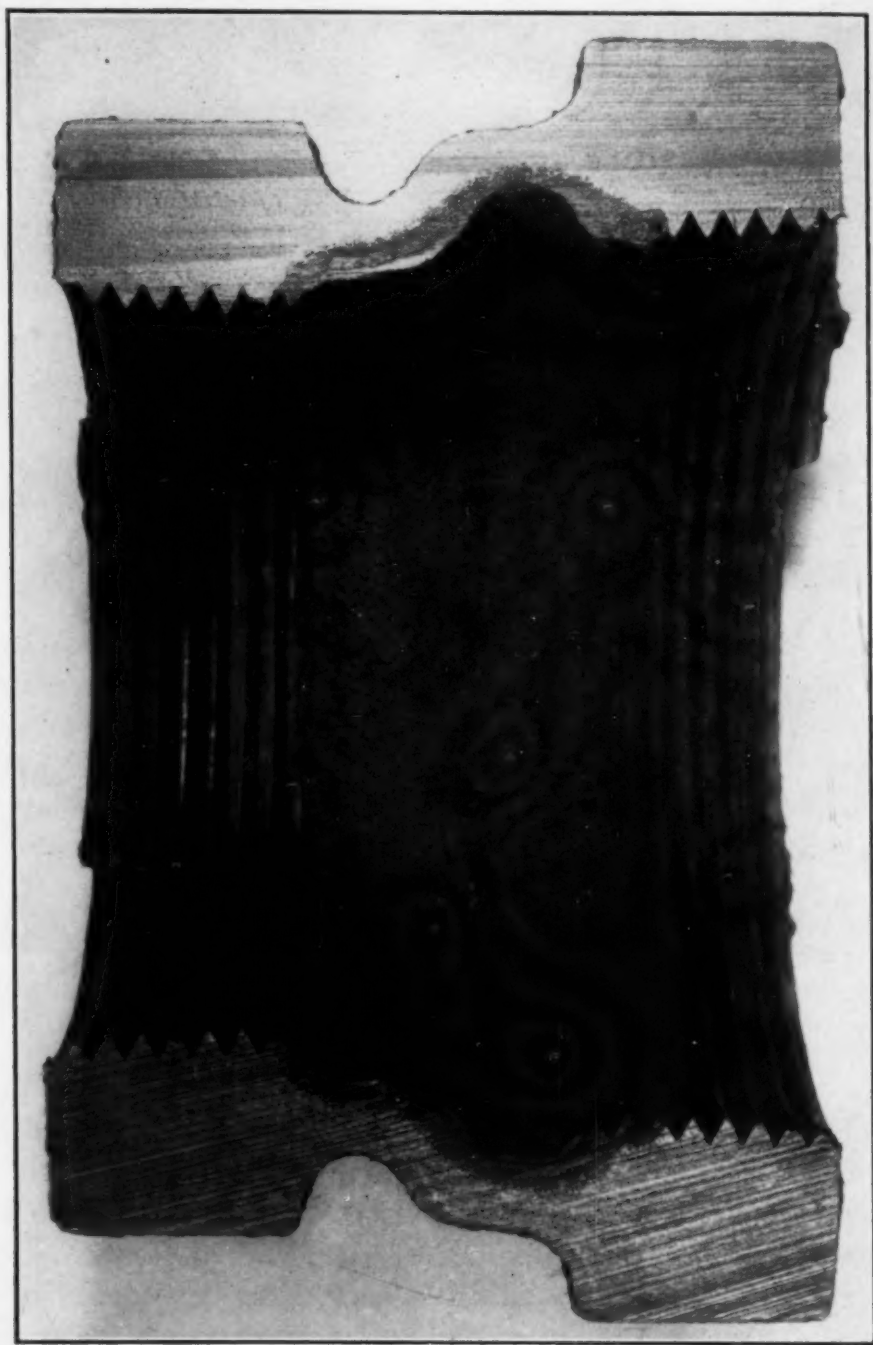


Fig. 3—Macrosection of Fitting. Attacked Portion Etched Darker.

However, the possible role of these bacteria in bringing about the corrosion of steel pipe has only been recently emphasized by R. F. Hadley (1), (2), (3).¹ In the past five years he has found that a

¹The figures appearing in parentheses refer to the bibliography appended to the paper.

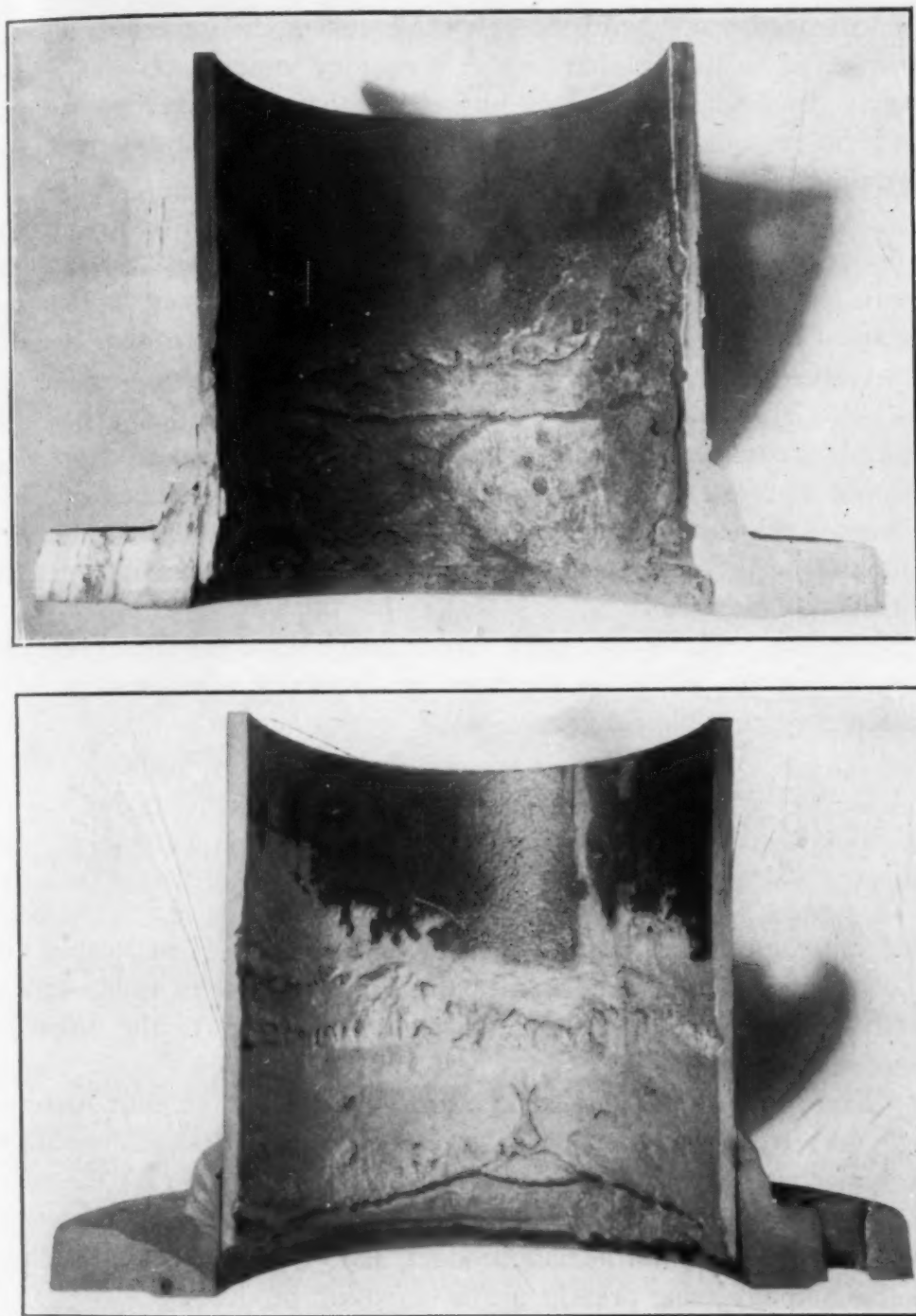


Fig. 4—Corrosion of Pipe Section Welded to Flange. (Upper) Unetched. (Lower) Macroetched.

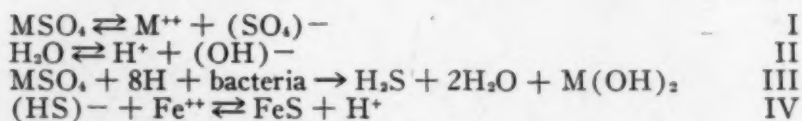
large part of his Company's corrosion of underground pipes was apparently due to sulphur bacteria. Hadley has described the bacteriological methods employed in demonstrating sulphur bacteria in

the corroded products of steel pipe, as well as the experimental production of such corrosion in the laboratory under controlled conditions. In field studies, it is interesting that this investigator finds bacteria responsible for from 50 to 80 per cent of pipe corrosion in certain Ohio Counties.

A simple and practical test for bacteriological action of the sulphur reducing type has been suggested by Hadley. When the corrosion products are acidulated with HCl, if H_2S can be detected by smell or reaction with lead acetate, Hadley presumes that bacteria are responsible.

P. Ganser (4) of the Philadelphia Electric Company has also described corrosion of buried gas pipes, and has demonstrated that sulphur bacteria were causing the trouble. W. J. O'Connell (5) has discussed the characteristics of microbiological deposits in water circuits in considerable detail and has included an extensive bibliography on sulphur bacteria.

On the basis of the work which has been done it is generally agreed that the following reactions are involved when sulphur bacteria are responsible for corrosion:



The sulphur bacteria are responsible for Reaction III and cause the sulphate radical to be reduced to the sulphide. There is likewise a further step which may be involved which converts the sulphide to free sulphur.

From this it follows that if corrosion is due to sulphur bacteria then (A) treating the corroded products with HCl should produce H_2S , as stated by Hadley, because of the FeS present, (B) the odor of H_2S should be present in the exhaust water from closed water lines, since it is an intermediate product, and (C) there is a possibility of free sulphur being present in the corrosion products.

EXAMINATION OF WATER SYSTEM

With these facts in mind a complete inspection was made of the water system throughout the steel mill and the following evidence

obtained to substantiate the belief that corrosion was due to sulphur bacteria:

1. The presence of free sulphur and sulphides in the corroded products but not in the water itself.
2. The odor of H_2S in the exhaust cooling water of each of the electric and open hearth melting furnaces.
3. The formation of H_2S when HCl is added to the corrosion products.
4. The odor of H_2S when the pumping equipment is dismantled at the well.
5. The fact that corrosion started at the water entrance of the plant and is gradually spreading throughout the entire mill.
6. The fact that corrosion is steadily getting worse even with the same source of water.
7. The fact that the analysis of the city water is nearly identical to that of the mill and yet caused no marked corrosion. The city water is, however, chlorinated and this kills these particular bacteria.
8. The fact that this bacteria has, according to Hadley, been found in the following nearby counties of Ohio: Columbiana, Mahoning, Portage and Summit.

While the above findings were strong evidence that sulphate-reducing bacteria were active, it was believed advisable to definitely determine the actual presence of these bacteria and reproduce this type of attack in the laboratory.

BACTERIOLOGICAL EXAMINATION

Various tests were employed to obtain direct evidence of the presence in the corrosion product and water of bacteria with ability to reduce sulphates to sulphides.

A direct microscopic examination of the corrosion product revealed bacteria. These varied in size, form and staining characteristics. Often a filament of bacteria would contain organisms 0.8 to 1.0 by 2 microns in size and staining Gram negative² at one end while at the other extremity would be found organisms 2 by 8 microns in size and staining irregularly with nonstaining spaces within the cells. Also smaller curved, single forms were noted. These latter forms are to be noted in Fig. 5. Similar bacteria were demonstrated by

²A bacteriological term indicating that the organism did not retain a basic stain when decolorized procedures were employed.

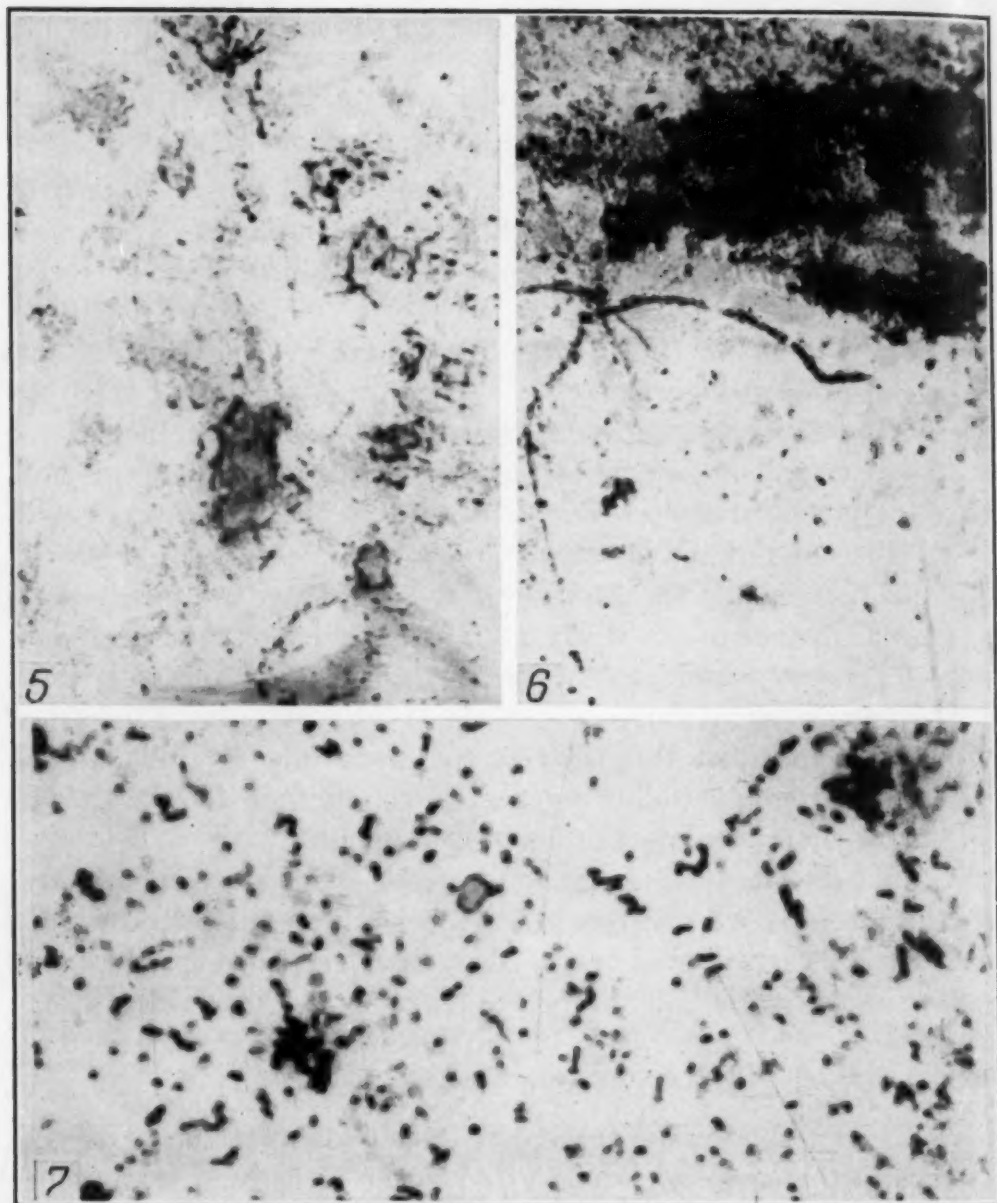


Fig. 5—Small, Single Bacteria in Background of Corrosion Products. $\times 600$.

Fig. 6—Filamentous Forms of Bacteria and Debris from Centrifuged Sediment of Cooling Water. $\times 600$.

Fig. 7—Bacteria Grown from Synthetic Sulphate Media Inoculated With Cooling Water. $\times 1200$.

direct examination of the sediment collected by centrifuging 500 cubic centimeters of well water. The filamentous forms obtained from the water are pictured in Fig. 6.

It can be safely stated that these findings are compatible with the morphological characteristics of the "sulphur group" of bacteria. But morphological characteristics are not adequate criteria for posi-

tively identifying organisms as sulphate-reducing bacteria. For this purpose more direct evidence is indicated.

In order to determine whether or not the corrosion product or water from the cooling system contained bacteria which would produce sulphides from sulphates, culture methods were used. Tubes of sterilized cooling water or the synthetic media, described by Hadley (3) with sulphur present as sulphate and carbon as lactate, were inoculated with varying amounts of corrosion product of various water samples. In some of the inoculated tubes the media was covered with sterile mineral oil to insure anaerobic conditions, since it is well recognized that this biological reduction of sulphate takes place in the absence of molecular oxygen. The cultures were incubated at 55 to 60 degrees Fahr. (10 to 15 degrees Cent.) for 2 to 3 weeks and then examined.

The corrosion product employed in these tests had been standing exposed to air for too long a period to be an entirely satisfactory sample. However, in about 10 per cent of the oil covered cultures a black deposit formed on an iron nail present in the inoculated water or media during the growth period. When such a nail was immersed in 10 per cent HCl the deposit was immediately acted upon and a resulting odor of H_2S was detected.

Small, slightly curved Gram negative rods were demonstrated in such cultures, Fig. 7. Thus the reduction of sulphate to sulphide has been demonstrated to be associated with the growth of bacteria present in the corrosion product and water of the cooling system. No attempt has been made so far to identify the species of the organisms involved, but this phase of the work is being continued.

CONCLUSIONS

On the basis of these findings, it is believed that the sulphate-reducing bacteria are the primary cause of the severe corrosion encountered in the water cooling pipe lines and the enclosed metal parts of the well. Since these bacteria are anaerobic and hence very susceptible to increased oxidation potentials, chlorination of the water should be an ideal treatment for eliminating this attack.

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DISCUSSION

Written Discussion: By A. H. Thomas, chief chemist, Research Laboratories, The American Rolling Mill Co., Middletown, Ohio.

The paper by Drs. Clark and Nungester is a valuable contribution to the knowledge of corrosion in underwater conditions. The data these authors have accumulated confirm the experience we have had during the past several years in the ARMCO plant at Middletown, Ohio. Where corrosion was caused either by the sulphate reducing or by the so-called "iron-consuming bacteria," the difficulty has been overcome by chlorine treatment of the water.

At our Middletown Division we were confronted for years by severe sulphidic corrosion of lines carrying water from about ten drilled wells located on our property. The water from these wells at all times had a distinct odor of hydrogen sulphide gas, which was a subject of constant complaint by the workmen in the plant. When the corrosion had progressed to the stage where it was necessary to replace the line, the pipe was found to be encrusted on the inside surfaces with a heavy black deposit that proved to be chiefly iron (ferrous) sulphide.

Not only did we encounter severe corrosion of our water piping, but we were bothered considerably by the stoppage of high pressure sprays on our mills. At one time we thought this was caused by iron precipitated from the water. Investigation revealed that the stoppage was due to excessive growths of iron-consuming bacteria such as crenothrix, leptothrix, spirophyllum and coccobacilli. These excessive growths would become dislodged and clog the spray nozzles, resulting in serious and expensive delays of production. The sulphidic corrosion that occurred in the pipe lines was without question the work of sulphate-reducing bacteria of the disulphurican group.

The condition was studied by our Research Laboratories in cooperation with Wallace and Tiernan Company. After the cause was determined we installed chlorination equipment. Since that time we have had no trouble with corrosion or stoppage of the high pressure sprays. The hydrogen sulphide odor also disappeared.

A somewhat similar condition was encountered at our division in Ashland, Kentucky, where river water was used. It likewise resulted in stoppage of sprays, which vanished following installation of chlorination equipment.

We also encountered an unusual failure in the case of a water pipe line installed near Uvalda, Texas. It began to show leaks after about two years' service. Mineral analysis of the water indicated it to be noncorrosive, but it

was characterized by the presence of 290 parts per million of sulphates. The pipe, which was removed from the line and examined in the laboratory, showed the presence of heavy deposits of iron sulphide, suggesting that the fairly high sulphate content was ideal for the growth and propagation of sulphate-reducing bacteria of the disulphurican group.

To study the functioning of these organisms, a fairly large scale laboratory experiment was carried on in the Research Laboratories with water from a special well. The water as it left the well had a dissolved oxygen content of 0.3 parts per million and was infested with crenothrix, leptothrix, spirophyllum, and coccobacilli. It was aerated to vary the dissolved oxygen content and immersion tests were made using clean samples of steel. After a relatively short period it was noted that there was a radical difference in the amount of apparent rust formation, the largest accumulation being present on the samples immersed in the water direct from the well with the least dissolved oxygen (0.3 parts per million). The amount of deposit decreased as the dissolved oxygen content was increased. In the water of low oxygen concentration this coating of rust was slightly fluffy and had the appearance of some form of algae, while at the highest oxygen concentration (9.0 parts per million), the deposits were more dense and compact and more nearly normal in appearance.

Bacteriological examinations made by Wallace and Tiernan Company indicated that the leptothrix was the least tolerant of oxygen, the spirophyllum more so, while the crenothrix and coccobacilli were the most tolerant or hardy. After the oxygen content of the water had increased to above 3.0 parts per million the leptothrix disappeared, while the spirophyllum went after the oxygen content had increased to 6.0 parts per million. At 9 parts per million oxygen crenothrix still flourished with a small amount of spirophyllum and a scant growth of coccobacilli. These data told us that aeration of the water was instrumental in preventing the growth of certain types of these organisms.

Treating the low oxygen water with small residual amounts of chlorine dissipated the entire accumulation after three days' treatment and prevented the formation of other deposits. This in itself was a practical demonstration of the efficacy of the chlorine treatment.

Since we encountered this effect of bacteria on the corrosion of iron and steel under water, we feel that ordinary mineral analysis of water, including the Langlier Index, does not give an absolute indication of whether or not such a water is corrosive. If after mineral analysis the water is believed to be non-corrosive, a bacteriological examination should be made to make certain that organisms of the type described above are not present. If they are, corrosive conditions may be anticipated and the water supply should be treated with chlorine.

Our detailed experiences were related in a paper entitled "Role of Bacteria in Corrosion," delivered at the Second Water Conference of the Engineers' Society of Western Pennsylvania, November, 1941. We believe that the relation of such types of bacteria to water troubles merits extensive study by all persons interested in underwater corrosion. The work of Drs. Clark and Nungesser should be instrumental in stimulating such investigations. They should be congratulated on their thorough study of the condition at the Timken Plant

and the remedies taken to eliminate the severe corrosion they have encountered in their installation.

Written Discussion: By Everett P. Partridge, director of research, Hall Laboratories, Inc., Pittsburgh.

A logical argument pointing to sulphate-reducing bacteria as the major factor in the corrosion in the water system of the steel plant of the Timken Roller Bearing Company has been presented by the authors. One can only speculate a little concerning the origin of these organisms and the reason for the accumulation in the well and in the distribution system.

The sulphate-reducing bacteria presumably must be present in the underground stratum through which the water percolates. Whether lodged on the surface of mineral particles or suspended in the water, one would expect them to carry on continuously their peculiar chemical process of reducing sulphate ions in the water to sulphide ions. If there were enough of these organisms busy underground, the water taken directly from the well should have the particularly unpleasant smell of hydrogen sulphide. That it does not may simply indicate that the ratio of sulphate-reducing bacteria to water flowing is very small underground.

Since the odor of hydrogen sulphide is apparent at various points in the system, the next inference must be that, for some reason, the sulphate-reducing bacteria must have become fixed and must have multiplied tremendously in the well and in the pipe lines.

What gave the bacteria a foothold on the steel surfaces which they were unable to gain on the mineral particles underground? Perhaps the answer lies in the film of oxide which inevitably develops on a steel surface in contact with water. Had there been no initial corrosion in the distribution system, perhaps there might have been no progressive accumulation of sulphate-reducing bacteria.

Turning from the academic to the practical, the authors' suggestion of chlorination of the water is proper. In case chlorine is not available, it seems possible that the sulphate-reducing bacteria or at least the hydrogen sulphide produced by them might be destroyed simply by aeration of the water. Pumping air through a diffuser plate into the water at the bottom of the well would be one means of applying oxygen.

If chlorine is available, practical trials over a period of time may show that intermittent dosage will suffice to keep the sulphate-reducing bacteria under control. In fact, dosing the water at intervals with a relatively high concentration of chlorine might prove both more effective and more economical than continuous feed at a lower level.

Our analyses of the underground water which supplies both the Timken well and the city of Canton indicate that more than 2.5 pounds of the hydrated oxides of iron and manganese will be precipitated from each million pounds of water chlorinated or aerated in the attempt to eliminate sulphate-reducing bacteria. To obviate the deposition of this material in the system, it is possible that Threshold Treatment with a few parts per million of molecularly dehydrated sodium phosphate glass, prior to the point of introduction of the oxidizing agent, will be necessary.

Written Discussion: By V. V. Kendall, corrosion engineer, National Tube Co., United States Steel Corporation Subsidiary, Pittsburgh.

The authors are to be commended for a most interesting and timely paper. It is now very well established that sulphate-reducing bacteria are responsible for corrosion in the soil to a much greater extent than was believed possible a few years ago. Since these bacteria are anaerobic, i.e., thrive in the absence of oxygen, we would not expect them to develop in water pipes except under unusual conditions. A deep well supply would come from a strata which we would assume would have a deficiency of oxygen and if it were piped directly to the distribution center without exposure to the air, the bacteria could continue their development. If, however, the water is filtered or treated, with incidental exposure to air, most of the bacteria would be killed and no trouble should be anticipated. Therefore, we would not expect corrosion due to this type of bacteria in municipal water supplies or industrial plants where the water is aerated or treated before using. In cases of corrosion in installations, such as cooling water for condensers, where the water is used direct from the source, these bacteria should be considered as a possible cause of the trouble.

In this connection, the question naturally arises as to the amount of oxygen that these bacteria can tolerate and how long they can survive after exposure to air, such as flowing over a weir or through a filter bed. In a municipal supply obtained from wells, are the usual methods of treatment, such as lime followed by chlorine, sufficient to prevent their development in the distribution system? The authors may possibly have some data on these questions.

The anaerobic sulphate-reducing bacteria should not be confused with the aerobic type of bacteria that have been known for years. The aerobic bacteria require iron to sustain growth but do not attack the iron directly. Their contribution to the corrosion problem seems to be in the building up of tubercles with consequent clogging of the pipe.

Written Discussion: By Carl Zapffe, Jr., research metallurgist, Battelle Memorial Institute, Columbus, Ohio.

The research by Clark and Nungester on corrosion and deposition by bacteria in water pipes in an industrial plant brings to my mind a quite parallel work by my father, Carl Zapffe, Sr., which bears on the destructive power of micro-organisms. His work was also prompted by economic reasons, but it resulted in new scientific values as well.

While serving in performance of a civic duty as President of the Water and Light Board, at Brainerd, Minn., Zapffe, Sr., became confronted with an ever increasing and aggravating problem of sludge accumulation and encrustation in the water mains and service lines of a wholly new system and a deep-well supply that he had fostered. To relieve that trouble, flushing mains once a month, at night, with high pressure and through manipulated circuits was tried for a whole year but proved inadequate in clearing the mains. It speeded clogging of the service lines. The precipitate was a mixture of the oxides of manganese and iron, mostly the former which was learned to be an exceedingly troublesome substance.

His studies of causes led to conclusions similar to those arrived at by the present authors. A biochemical process was involved, and it was of profound

significance because it gave the clue to an inorganic process which was speedier and could be regulated. There being no precedents of practical value available anywhere and the literature being found unsuitable, he undertook experimentation and worked it eventually on a very large scale. After 2 years he completed and patented not only a process but designed the first removal plant ever built, costing the city \$65,000. This plant has now been operating for 12 years and it performs as perfectly today as when first erected. The mains never had again to be flushed, and never again was it necessary to replace service lines due to encrustations. Water coloration on house fixtures has also been eliminated.

The whole idea is to extract the manganese and the iron in a building and not let them get into the mains. The accompanying sketch illustrates the

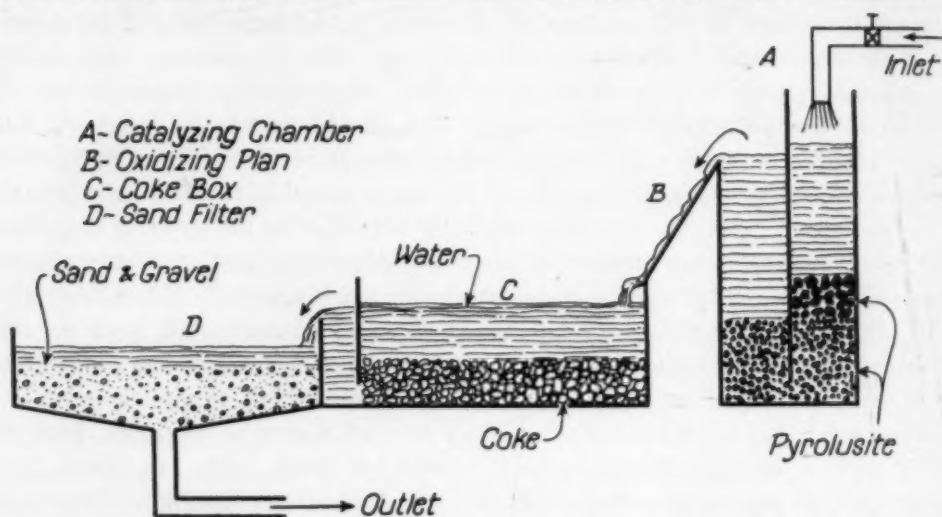


Fig. A—Sketch Illustrating the Flow of the Water Through the Several Units Comprising the Plant Used at Brainerd, Minn.

movement of the water through the several units. Essentially, these units combine the same principle in the organic and inorganic realms. In the organic, the bacteria are actually put to work in an environment suitable to their life processes, which, in practice, facilitates the deposition of the oxides of manganese and iron. Iron is ever quick to oxidize and easy to remove, but manganese is resistant and, as it were, has the iron to combat; therefore, the inorganic is applied, like an auxiliary force, to expedite the whole process.

The bacteria involved are nontoxic and their products are nontoxic and need no counter treatment on that score. Clark and Nungester use chlorine to kill; Zapffe has ever resisted all proposals made to have chlorine applied in the city water, because his purpose is to protect his protégés and use them. The thread bacteria most potent in this work are *crenotherix polyspora* Cohn, *leptothrix ochracea* Kützing, and *spirophyllum ferrugineum* Ellis. They are heavy feeders on manganese salts as well as on iron salts. Other bacteria attacking only iron are also present.

The fresh water is pumped from the wells into a bed of finely-ground pyrolusite (mainly MnO_2) which performs inorganically as a catalyst and speeds up the entire job. The dissolved bicarbonates are thus disassociated,

to be followed by the aeration so noted by Clark and Nungester as also a prerequisite in their work. Next, a slight alkalinity is needed; this the bacteria help to supply, but also crushed basic rocks and coke are used to assure having such a condition at all times. A pH of 7.1 or 7.2 is sufficient. In the deep bed of coke used the bacteria find the ideal home and work-ground, and here about 80 per cent or more of all oxides formed after oxidation become fixed and entrapped. Sand beds perform as a final filter. All beds are backwashed once a month.

Combining all these forces has led to spectacular success. It is a surprisingly inexpensive treatment and needs no technical supervisor to govern its operation. The tasks performed by these little scamps was found to be so profound and monumental that it led to formulating a new theory for the origin of certain types of Minnesota iron-bearing formations; and investigators in the field of geology who have made quantitative tests on chemical reactions involved support the sufficiency of the process in very many respects. It is, therefore, easy to understand that a pipe system in an industrial plant can be made to suffer in severe fashion by these microscopic organisms, and that bacteria need not be looked upon as mere possibilities, or as having only scientific interest.

For any who may be interested in details on the subject and bibliography I suggest referring to the following three publications:

Carl Zapffe, "Deposition of Manganese," *Economic Geology*, Vol. 26, No. 8, 1931, p. 799-832.

Carl Zapffe, "The History of Manganese in Water Supplies and Methods for Its Removal," *American Water Works Journal*, Vol. 25, No. 5, 1933, p. 655-676.

Carl Zapffe, "Catalysis and Its Bearing on Origin of Lake Superior Iron-Bearing Formations," *Economic Geology*, Vol. 28, No. 8, 1933, p. 751-772.

Authors' Reply

We appreciate the interest shown in this paper and the several discussions which have been offered and hope that, as a result of this, corrosion due to sulphate-reducing bacteria may be more readily recognized.

As Mr. Kendall stated, it has long been realized that sulphate-reducing bacteria are often responsible for corrosion of steel exposed to soil but instances of where attack of this type has occurred on the inner wall of pipe on the water side are not as common. Evidently, however, Mr. Thomas' experiences in the various plants of the American Rolling Mills were very similar to ours. In our case, as well as in his, the condition of the water was such that it could be used directly as pumped from the well without any treatment or aeration and consequently anaerobic conditions existed in the system, thus making possible the growth and activity of the sulphate-reducing bacteria. In regard to Mr. Kendall's question as to the amount of oxygen these bacteria can withstand, we have as yet no definite information. However, Mr. Thomas, in his discussion, has given some data on this subject.

It was not until our own work had been completed that we heard of the similar problem at the American Rolling Mills and of their successful elimina-

tion of the corrosion by chlorination. We were very pleased to receive Mr. Thomas' analysis and solution of their problem and to find how the work of each had substantiated that of the other.

Dr. Partridge's comments with respect to the origin of these bacteria and the reasons for their accumulation in the system are most interesting as are his thoughts with respect to other factors which may have to be considered in the treatment of the water. If found necessary his suggestions will certainly be put into practice.

Dr. Zapffe's description of the conditions encountered in Minnesota, and the equipment developed for handling this particular problem, is very interesting but the type of bacteria with which he dealt was not of the sulphate-reducing type, which is the one in which this paper is primarily interested.

In closing it should again be emphasized that analysis of water as ordinarily reported, is not necessarily a measure of its possible corrosiveness. It might also be necessary to determine what type bacteria are present, especially if the water is to be used directly as it is pumped from a well or stagnant pond.

EFFECT OF ELEMENTS IN SOLID SOLUTION ON HARDNESS AND RESPONSE TO HEAT TREATMENT OF IRON BINARY ALLOYS

BY CHARLES R. AUSTIN

Abstract

Few data are available on solid solution hardening and reaction to heat treatment of iron binary solid solutions.

The following elements were added to iron in amounts ranging from 0.5 to 5 per cent and they are listed in order of increasing potency of hardening in the fully annealed alloys: Chromium, cobalt, nickel, manganese, molybdenum and silicon.

The hardening effect in alloys cooled rapidly from above the critical may be quite different. Thus while quenching has a relatively minor hardening effect on the 5 per cent nickel alloy, considerable hardening is obtained on quenching an iron-chromium binary alloy of similar chromium content.

The effect of heat treatment on technically pure iron has also been investigated, and the effects of the different elements on solid solution hardening have been considered in relation to type of lattice structure, lattice constant, atomic radius and maximum solubility of the added element.

DESPITE the importance of the effect of alloy elements in solid solution on the hardness of ferrite, few quantitative data appear in the literature. Similarly, little information is available on the manner in which such alloys react to heat treatment. In order to permit the development of a comprehensive investigation on various properties of iron as modified by the presence of certain elements in solid solution several binary alloys were prepared for the author's laboratory by Mr. P. H. Brace of The Westinghouse Electric and Manufacturing Co. The present paper provides data on the effect of varying amounts of elements in solid solution on the hardness of pure iron in the softest state of the alloys, and demonstrates their markedly different reaction to heat treatment.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. The author, Charles R. Austin, is professor of metallurgy, Pennsylvania State College, State College, Pa. Manuscript received May 6, 1942.

The information in the literature on pure iron, although somewhat contradictory, seems to indicate that quenching from above the critical does not markedly affect the mechanical properties (1).^{*} The hardness of commercially pure iron, such as ingot iron, is increased by quenching (2). Sykes (3) found that the hardness of alloys containing up to 3.5 per cent molybdenum depended on the rate of cooling. On slow cooling the increase in hardness was a linear function of the molybdenum content, whereas on water quenching from the gamma phase field the hardness showed a maximum with 2 per cent molybdenum.

Several investigations have demonstrated the progressive increase in hardness of iron by the addition of nickel, in the annealed state, but the results of studies on the susceptibility of the alloys to further hardening by heat treatment are confusing (4).

Some work has been done on the effect of silicon (5) on the hardness of iron, but apparently no data are available for cobalt. It has been reported that in the quenching of low manganese content iron-manganese alloys the alloying element tends to accelerate rather than inhibit the transformation to the lower temperature phases (6). Bain (7) states that iron-chromium alloys containing less than about 12.8 per cent chromium, which exhibit allotropy, are definitely hardened by quenching from temperatures establishing the iron solid solution.

In discussing the solid solution hardening effect on pure iron Bain (8) recently wrote "surprisingly little is known of the effects of the alloying elements dissolved in ferrite and this includes even hardness and tensile properties." Reference should also be made to the "meager data assembled and carefully considered as to the most probable values," which Bain has included in the cited reference.

PREPARATION OF THE ALLOYS

The ingots were made with hydrogen-annealed electrolytic iron melted in magnesia crucibles by means of a large high frequency induction unit. The melts were prepared under purified dry hydrogen, frozen in the furnace, reheated to just above melting and again allowed to freeze in the furnace. The object of the procedure was to minimize porosity dependent on the release of hydrogen from solution during solidification.

^{*}The figures appearing in parentheses pertain to the references appended to this paper.

The ingots were then forged to about 2-inch square sections and rolled to $\frac{3}{8}$ -inch diameter bar stock. Half of this bar stock (from the bottom end of the ingot) was rolled down to $\frac{5}{16}$ -inch diameter. The bars were finished by centerless grinding.

CHEMICAL ANALYSIS OF THE ALLOYS

It will be noted in Table I that the alloy additions include manganese, nickel, chromium, cobalt, molybdenum, and silicon. It was initially proposed to have three alloys for each element addition, containing 0.5, 1.0, and 5.0 per cent respectively. However, all the

Table I
Chemical Analysis of the Iron Binary Alloys

Sample	Marked	Mn	C	P	S	Co	Mo	Ni	Cr	Si
1	3602	0.03	0.02	0.010	0.013	0.005	0.004	0.032	0.003	0.003
2	3574	0.03	0.03	0.010	0.011	0.005	0.004	0.57	0.003	0.004
3	3607	0.03	0.02	0.010	0.015	0.005	0.004	1.15	0.003	0.004
4	3677	0.03	0.02	0.010	0.016	0.005	0.004	4.83	0.003	0.004
5	3574	0.05	0.03	0.011	0.011	0.005	0.004	0.032	0.45	0.012
6	3610	0.03	0.02	0.010	0.013	0.005	0.004	0.034	0.99	0.004
7	3682	0.03	0.03	0.012	0.015	0.005	0.004	0.023	4.83	0.008
8	3608	0.69	0.02	0.010	0.014	0.005	0.004	0.032	0.003	0.004
9	3678	1.33	0.06	0.011	0.020	0.005	0.004	0.030	0.003	0.004
10	3679	7.25	0.03	0.012	0.022	0.005	0.004	0.035	0.003	0.13
11	3609	0.03	0.02	0.012	0.014	0.52	0.004	0.037	0.003	0.004
12	3681	0.05	0.02	0.010	0.019	1.00	0.004	0.043	0.003	0.004
13	3680	0.03	0.02	0.012	0.015	5.08	0.004	0.08	0.003	0.004
14	3611	0.03	0.03	0.012	0.015	0.006	0.004	0.033	0.003	0.22
15	3683	0.03	0.02	0.011	0.018	0.005	0.004	0.032	0.0045	0.59
16	3700	0.03	0.02	0.010	0.012	0.005	0.004	0.055	0.003	1.21
17	3688	0.03	0.03	0.010	0.014	0.005	0.11	0.054	0.003	0.004
18	3690	0.03	0.03	0.010	0.014	0.005	0.54	0.023	0.003	0.004
19	3691	0.03	0.04	0.011	0.014	0.005	1.50	0.016	0.003	0.004

manganese alloys showed a markedly higher element content on analysis and this fact should be remembered when considering the experimental results. The maximum molybdenum content was 1.5 per cent and the maximum silicon content was 1.21 per cent. A 5 per cent silicon alloy was melted but it broke up under the hammer.

ACKNOWLEDGMENTS

The assistance of Dr. Miles K. Smith, Latrobe Electric Steel Co., in supervising the rolling and grinding operations was much appreciated. For the complete chemical analysis of the alloys we are indebted to E. J. Kaulfuss, Bethlehem Steel Co.

REACTION OF ALLOYS TO HEAT TREATMENT

Since all the alloys were ferritic solid solutions at subcritical

temperatures, and gamma solid solutions above 950 degrees Cent. (1740 degrees Fahr.), heating above the critical afforded a means of grain refinement and possible control of hardness as a result of rate of cooling. On the other hand complete softening of the alloys could be expected from annealing followed by slow cooling from some elevated temperature below the critical.

Accordingly all treatments studied commenced with a possible grain refinement by heating to 975 degrees Cent. (1785 degrees Fahr.) for 1 hour followed by various methods of cooling to room temperature, or to 650 degrees Cent. (1200 degrees Fahr.) where a second heat treatment was conducted as shown in Table II.

Table II
Annealing Treatments

Designation	1st Anneal		Method of Cooling	2nd Anneal		Method of Cooling
	Time	Temperature		Time	Temperature	
I	1 hr.	975° C.	Fur. cool to 650° C.	20 hrs.	650° C.	Furnace cool
II	1 hr.	975° C.	Fur. cool to room temp.			
III	1 hr.	975° C.	Fur. cool to 650° C.	20 hrs.	650° C.	Water quench
IV	1 hr.	975° C.	Air cool to room temp.			
V	1 hr.	975° C.	Water quench			

The results of heat treatment were studied from data obtained from Vickers Pyramid Hardness (V.P.N.) tests. Observations were also made on variations of grain size as a function of heat treatment.

The specimens used were about $\frac{3}{8}$ inch long and were cut from the $\frac{5}{16}$ -inch diameter centerless ground bar stock. All heat treatments were conducted in a moderate vacuum with temperatures accurately controlled to ± 1 degree Cent. After treatment the specimens were ground and polished through 000 paper before taking the Vickers hardness number with a 10-kilogram load maintained for 30 seconds. The complete data on the effect of the five different heat treatments on the hardness of the alloys were used to prepare the composite diagram shown in Fig. 1.

The following general observations can be drawn from these curves showing the relationship between the alloy addition and the Vickers pyramid hardness number for each of the six different alloys heat treated by each of the five different annealing treatments previously listed. Table II.

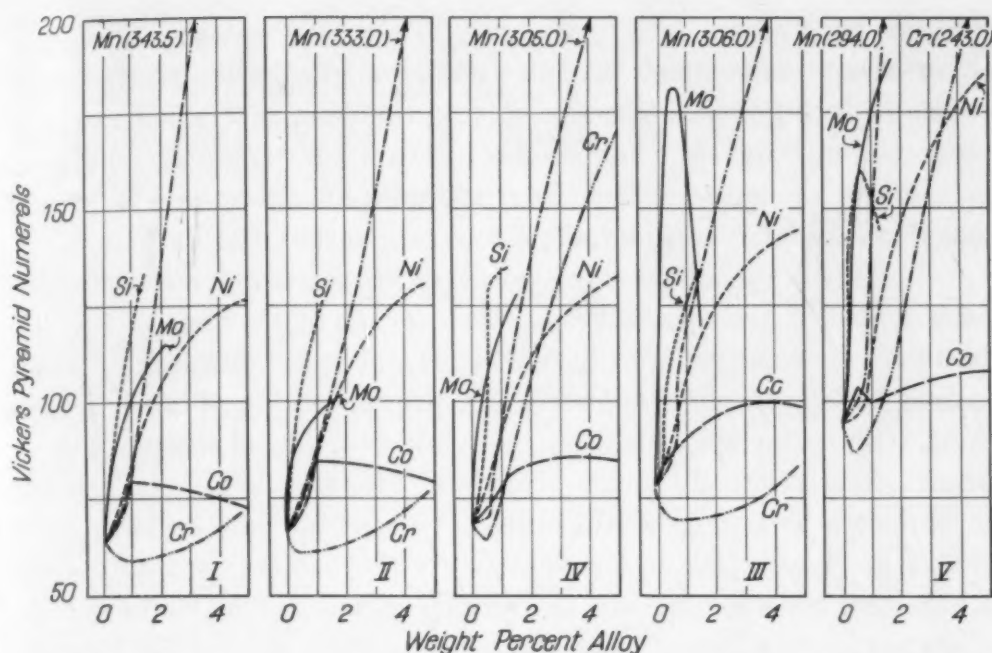


Fig. 1—Effect of Each of Five Different Heat Treatments (See Table II), on the Reaction of the Iron Binary Solid Solutions, as a Function of Weight Per Cent Added Element.

1. Commercially pure iron may be hardened by heat treatment. In the softest state the sample having a V.P.N. of 64.5 was subject to slight hardening on quenching from 650 degrees Cent. (1200 degrees Fahr.) (79.5 V.P.N.), and marked hardening on quenching from 950 degrees Cent. (1740 degrees Fahr.) (95 V.P.N.)

2. After slowly cooling the alloys to 650 degrees Cent. (1200 degrees Fahr.), subsequent change in treatment (Fig. 1, Curves I, II, III) had only a minor effect on the hardness obtained. The 0.54 per cent molybdenum alloy seems to provide an exception to this general observation since water quenching from 650 degrees Cent. (1200 degrees Fahr.) apparently markedly hardens the alloy. The results of two separate tests run on this alloy showed some disagreement, but the general trend was similar.

3. As regards the magnitude of the solid solution hardening effect as a function of amount of added element in the fully annealed alloys, some rather striking results were obtained. Silicon and molybdenum exhibit the most potent solid solution hardening on the fully annealed alloys. Manganese and nickel have a less marked effect for similar added weights per cent. It must be noted that the true position of the manganese curve is uncertain since the desired 5 per cent manganese alloy was found by

analysis to contain 7.25 per cent. This alloy passes through a phase change on cooling. Cobalt exhibits slight hardening, but chromium up to 1 per cent actually softens the iron, and it increases the hardness only slightly when present up to 5 per cent. This observation seems of interest since the addition of chromium is usually considered to have considerable effect as a ferrite hardener.

4. When the alloys are cooled more rapidly from above the critical, that is from the gamma phase (Curves IV and V, Fig. 1), the effect on solid solution hardness may be quite different. On air cooling small specimens from 975 degrees Cent. (1785 degrees Fahr.) the presence of silicon, molybdenum, nickel, manganese, or cobalt show relatively small quenching effects. With 0.5 per cent chromium a softening is still noted, while with 1 per cent the effect of this more rapid cooling rate begins to be evident, but with about 5 per cent considerable air hardening results. This highest chromium addition is found to be more potent than any of the elements studied, with the exception of manganese. It must be remembered however that alloys containing 5 per cent molybdenum or 5 per cent silicon were not available.

On water quenching from 975 degrees Cent. (1785 degrees Fahr.) the effects of rapid cooling are still more evident. However, the V.P.N. of the commercial iron can be increased from 65 to 95 by heat treatment, and this fact should be borne in mind in considering the individual effects of the various elements on quenched hardness.

For convenience of study the hardness data have been suitably grouped in Table III. The data recorded represent the averages of several observations. In one column will be found the hardness data which may be assumed to indicate the hardening effect, due to the alloy in solid solution, on quenching from 975 degrees Cent. (1785 degrees Fahr.). Since the hardness of the commercial iron was increased about 30 points by this treatment, compared with a slow cool representing dead softness (Treatments I or II), 30 units have been deducted from the observed hardness values (Treatment V) of each of the alloys.

From these data it may be noted that the addition of about 0.5 per cent nickel, chromium, manganese, or cobalt, 0.2 per cent silicon or 0.1 per cent molybdenum does not materially lead to an increase in solid solution hardening by water quenching. With as much as

Table III
Vickers Pyramid Hardness Numbers Obtained on the Binary Alloys after Different Heat Treatments

Vickers Pyramid Hardness Numbers										
Alloy No.		Wt. % Addition		As Rec.	I	II	III	IV	V	Diff. in Hardness Between WQ and FC from 975° C.
				1 Hr. 975° C. F.C.			1 Hour 975° C.			
				to 650° C.			to 650° C.			
				20 Hr. 650° C. Fe. Cool	Con- tinue to RT	20 Hr. 650° C. WQ	Air- Cool to RT.	Water Quench	Values for V Treatment Less 30 VPN	
1	100	Fe	106	64.5	67	79.5	69	95	65	0
2	0.57	Ni	99.5	70	71	83	70.5	96.5	66.5	- 3
3	1.15	Ni	137	88.5	89	111	97.5	118	88	0
4	4.83	Ni	146	126	131	145.5	131	185	155	+ 30
5	0.45	Cr	101	58	60	70	64.5	87.5	57.5	0
6	0.99	Cr	91.5	58.5	64	68	74.5	92	62	0
7	4.83	Cr	107	72	77	84.5	170	243	213	+ 140
8	0.69	Mn	120	81.5	80.5	96.5	81.5	104	74	- 7
9	1.33	Mn	133	97	94	128.5	113	191	161	+ 65
10	7.25	Mn	363	345	333	306	305	294	264	- 70
11	0.52	Co	131	75	74.5	87	73	104	74	0
12	1.0	Co	101	79	85.5	90.5	80	100	70	- 9
13	5.08	Co	97.5	72.5	79	100	84	109	79	- 7
14	0.22	Si	118	79	82.5	89.5	84	108	78	0
15	0.59	Si	129	93.5	111	116	130.5	160	130	+ 35
16	1.21	Si	146	127	125	133	135	146	116	- 10
17	0.11	Mo	110	74	76.5	95	79.5	109	79	+ 5
18	0.54	Mo	108	91.5	92.5	182	104	153	123	+ 30
19	1.5	Mo	115	110	99.5	120	128	186	156	+ 45

a 5 per cent addition of nickel or cobalt the change in hardness by heat treatment is small.

The most striking effects of increased cooling rate are observed in the alloys containing 5 per cent chromium or 1.5 per cent manganese, and particularly when a small addition of silicon (0.75 per cent) or molybdenum (0.5 or 1.5 per cent) was made to the commercial iron.

Since the information obtained in this study is to be utilized in further examination of the effects of the elements on the rate of work hardening and on temperature softening, observations were also made on grain size characteristics.

Grain size measurements were made on all the alloys in the as-received condition and after the heat treatment (I) which generally had the maximum effect on softening. These data have been compiled in Table IV.

For the investigation of work-hardening and temperature softening an effort is being made to have all of the alloys with approximately similar grain sizes arbitrarily chosen as ranging between No. 4 and No. 6 ASTM grain size.

In the as-received condition the grain size of the alloys did not vary materially from these chosen limits with the exception of that

Table IV
Effect of Varying Heat Treatment on A.S.T.M. Grain Size of the Alloys
(V.P.N. Hardness Shown in Parentheses)

Alloy No.	Wt. % Addition	As Rec'd	A.S.T.M. Grain Size and V.P.N.					
			Large (106)	1 Hr. 975° C. 20 Hrs. 650° C. Furn. Cool (I)	20 Hrs. 650° C. Furn. Cool	1 Hr. 1100° C. 20 Hrs. 500° C. 600° C. Furn. Cool	1 Hr. 920° C. 20 Hrs. 700° C. Furn. Cool	20 Hrs. 700° C. Furn. Cool
1	100 Fe		Large (106)	<1 (64.5)	<1		<1	
2	0.57 Ni		6½ (99.5)	1 (70)	6		1	
3	1.15 Ni		3 (137)	3 (88.5)	.		.	
4	4.83 Ni		7 (146)	7 (126)	.	6½ (121)	.	
5	0.45 Cr		6½ (101)	1 (58)	6		1	
6	0.99 Cr		2 (91.5)	2½ (58.5)	.		.	
7	4.83 Cr		8 (107)	4½ (72)	.	3½ (70.5)	.	
8	0.69 Mn		3½ (120)	2½ (81.5)	.		.	
9	1.33 Mn		6 (133)	6½ (97)	.	4½ (99.5)	.	6 (98.5)
10	7.25 Mn		10 (363)	8 (343)	.	5 (342)	.	7 (340)
11	0.52 Co		5 (131)	<1 (71.5)	5		<1	
12	1.0 Co		5 (101)	2½ (79)	.		.	
13	5.08 Co		5 (97.5)	3 (72.5)	.		.	
14	0.22 Si		4 (118)	1 (79)	4½ (87.6)		<1	
15	0.59 Si		8 (129)	4½ (93.5)	.	3 (109)	.	
16	1.21 Si		5½ (146)	<1 (127)	5		<1	
17	0.11 Mo		6½ (110)	3 (74)	.		.	
18	0.54 Mo		7 (108)	3½ (91.5)	.		.	
19	1.5 Mo		7 (115)	5½ (110)	.	4 (103)	.	

of pure iron (coarser than grain size No. 1) and of the 5 per cent chromium and 0.75 per cent silicon (grain size No. 8) alloys. It is suggested that the 7.5 per cent manganese (grain size No. 10) cannot be strictly regarded as a simple solid solution.

The author acknowledges the helpful assistance of Shaoteh Yuan and Dr. F. R. Morral in collection of the data.

DISCUSSION

A clear picture of the response of each of the alloys to hardening by heat treatment can be obtained from the series of plots of Vickers hardness numbers as a function of alloying element for each of the five treatments studied (Fig. 1). The relative effects of these five heat treatments on the hardness of commercially pure iron containing approximately 0.5, 1 or 5 per cent of the elements are illustrated in the composite Fig. 2.

Considering the effects of increasing amounts of added element on the solid solution hardness (Fig. 1) it is of interest to note the presence of a "hump" in the curves for cobalt, silicon and molybdenum. This maximum hardening effect, at concentrations below saturation, has been noted in the literature, for both the nickel and molybdenum-iron solid solutions. Thus Sykes (3) has pointed out

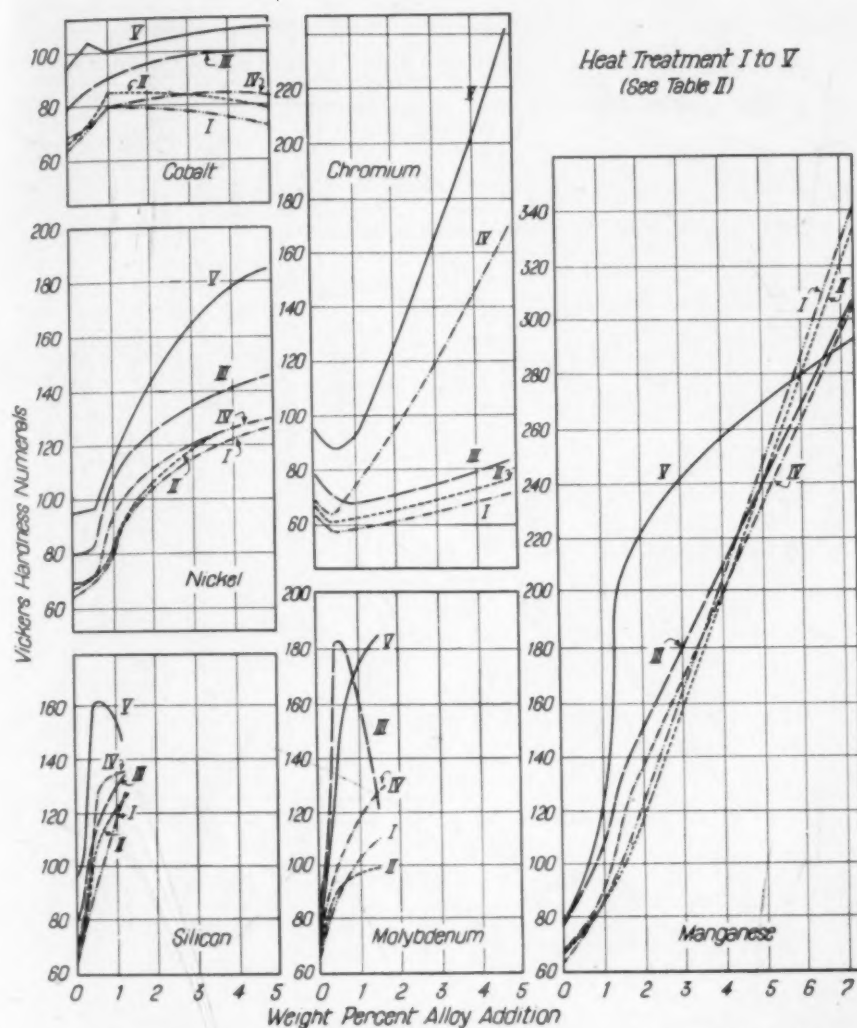


Fig. 2—Effect on Each of the Six Different Element Additions, of the Five Different Heat Treatments (See Table II), as Indicated by the Change in Hardness as a Function of Amount of Added Element.

that the rate of cooling iron-molybdenum alloys through the gamma region materially affects the hardness and that on quenching from 1450 degrees Cent. (2640 degrees Fahr.) a maximum or "hump" in the hardness-per cent element curve occurs at 2 per cent molybdenum.

The maximum for iron-nickel solid solutions (10) is found between 15 and 20 per cent nickel content with carbon varying between 0.05 and 0.07 per cent.

Each of the six sections of Fig. 2 shows the susceptibility of a given iron base solid solution to hardening, as a function of heat treatment and amount of alloying element. The cobalt alloys remain relatively soft independent of composition and heat treatment.

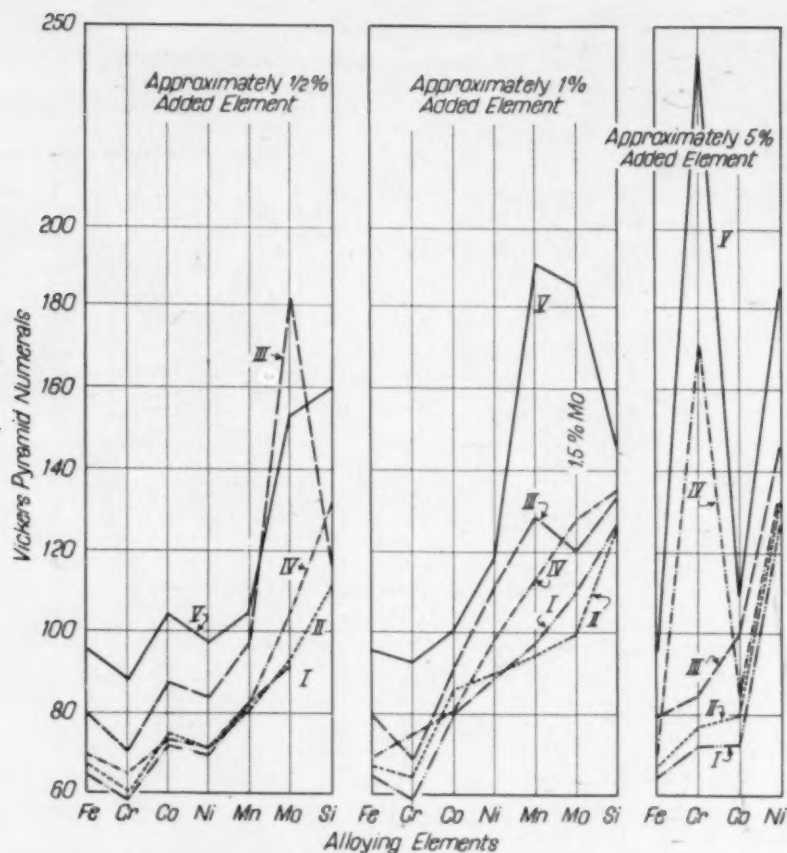


Fig. 3—Comparison of the Effects of 0.5 Per Cent, 1 Per Cent and 5 Per Cent Approximately of Each of the Added Elements on the Hardness of Iron as Modified by the Different Heat Treatments (Table II).

With nickel, silicon or molybdenum in solid solution any of the three treatments involving slow cooling to room temperature (I, II and IV) exhibit only minor differences in effect on hardness, whereas either of the water quenching treatments (III and V) reveal marked hardening of the alloys, even though one of these treatments (III) relates to water quenching from 650 degrees Cent. (1200 degrees Fahr.).

With the alloys containing 5 per cent chromium either water quenching or air cooling from 975 degrees Cent. (1785 degrees Fahr.) results in a significant hardening. This alloy is clearly air hardening. Thus this reaction to heat treatment is different from that observed in any of the alloys studied.

Fig. 3 shows the general relative potency of the elements as solid solution hardeners. The three sections of this diagram relate to approximately 0.5, 1 and 5 per cent element addition respectively.

While the particular heat treatments employed have effects of

varying magnitude, dependent on alloying element, the general order of increasing potency with respect to hardening may be listed as follows: Chromium, cobalt, nickel, manganese, molybdenum and silicon.

In Fig. 4 the curves suggested by Bain, and those obtained by

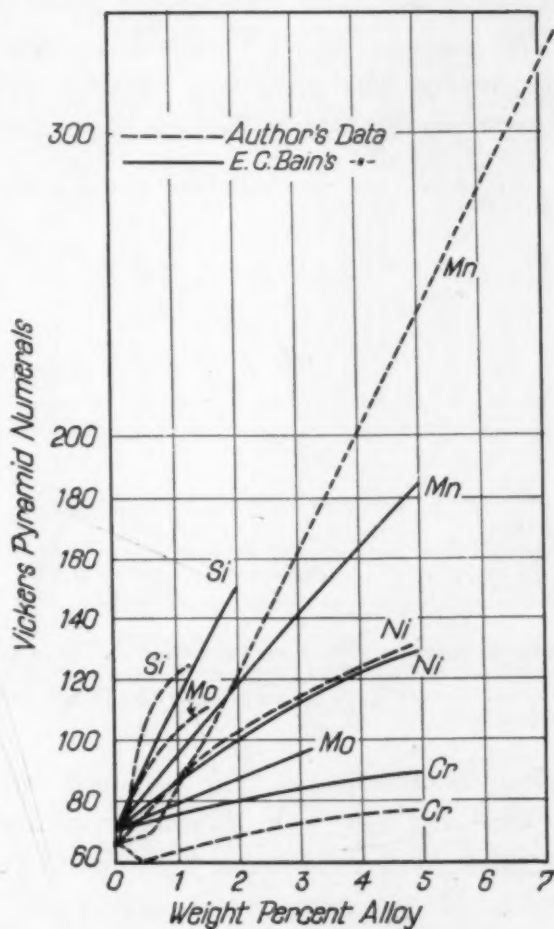


Fig. 4—Comparison of Data Suggested by Bain with that Obtained by the Author for Simple Solid Solution Hardening Effects of the Elements Nickel, Chromium, Manganese, Silicon and Molybdenum, Independent of the Increased Hardening Which May Be Effected by Rapid Cooling.

the present author, show the hardening effects of the various elements dissolved in iron. It is assumed that in both instances the alloys were annealed to the dead soft condition. Good agreement is found in the data for nickel and silicon and for manganese in the lower percentages. Bain also indicated that chromium would have limited hardening but does not forecast the actual softening ob-

tained in the present study. A marked difference in the indicated effect of molybdenum may be noted.

It has been pointed out that the hardness of the base metal iron is dependent on heat treatment. From the literature (11) data have been obtained for the lattice parameters of iron measured at temperatures ranging from 25 to 850 degrees Cent. (75 to 1560 degrees Fahr.). The average values obtained for the parameters on four samples of iron by two different investigators were plotted against the temperature at which the measurements were made.

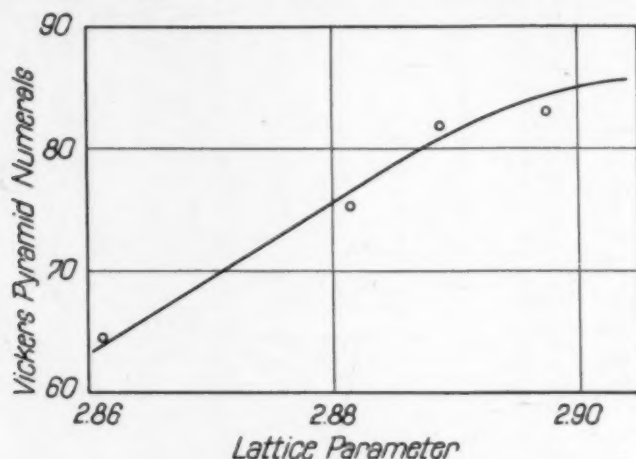


Fig. 5—Relation of Lattice Parameters of Pure Iron Obtained at Certain Elevated Temperatures with the Hardness Obtained on Quenching from Those Same Temperatures.

From this plot lattice parameters at 500, 650 and 850 degrees Cent. (930, 1200 and 1560 degrees Fahr.) were recorded, and plotted (Fig. 5) against the Vickers hardness numbers obtained after quenching specimens of the commercial iron from corresponding temperatures. There is of course little significance in extending the plot to 975 degrees Cent. (1785 degrees Fahr.) on account of the phase change from alpha to gamma iron which results in a sudden parameter increase from 2.90 to 3.64.

The relationship shown in Fig. 5 indicates that the hardness of iron upon quenching from below the critical point (A_3) increases approximately directly with the increase in the lattice parameter at quenching temperature. It may then be inferred that the progressive increase in hardness on quenching from higher temperatures is dependent on the retention of the parameter characteristic of the iron at quenching temperature. No density or X-ray measurements have been made to confirm this hypothesis.

Table V
Structure Type, Lattice Characteristics of the Added Element and Their Solid Solubility in Ferritic Iron

Element	Type of Structure	Lattice Constant	Atomic Radius*	Effects of Element in Solid Solution on Iron Lattice			Solid Solubility Weight, Per Cent		
				Wt. %	At. %	Parameter	Room Temp.	650° C.	975° C.
Fe	b.c.c.	2.861	1.26	2.8601
Co	c.p.h.	2.50	1.25	4.9	4.6	2.8604			
				7.7	7.3	2.8607			
				9.7	9.2	2.8606	80	75	Gamma
				3.11	2.96	2.8619	18	3½	Gamma
Ni	f.c.c.	3.517	1.25	6.00	5.73	2.8629			
				8.96	8.56	2.8629			
				2.1	1.97	2.8613			
				4.1	3.83	2.8624	33	37	Unlimited
Cr	b.c.c.	2.878	1.30	6.5	6.10	2.8637			
				8.4	7.89	2.8643			
				?	?	?	6	8	10
				3.56	6.5	2.857	14	14	17
Mo	b.c.c.	3.140	1.39	?	?	?			
Si	Diamond	5.41	1.172	7.11	13.2	2.845			
Mn	Complex	1.27	5	4.9	2.8638	14	6½	Gamma
				10	9.9	2.8675			

*Goldschmidt C. N. 12.

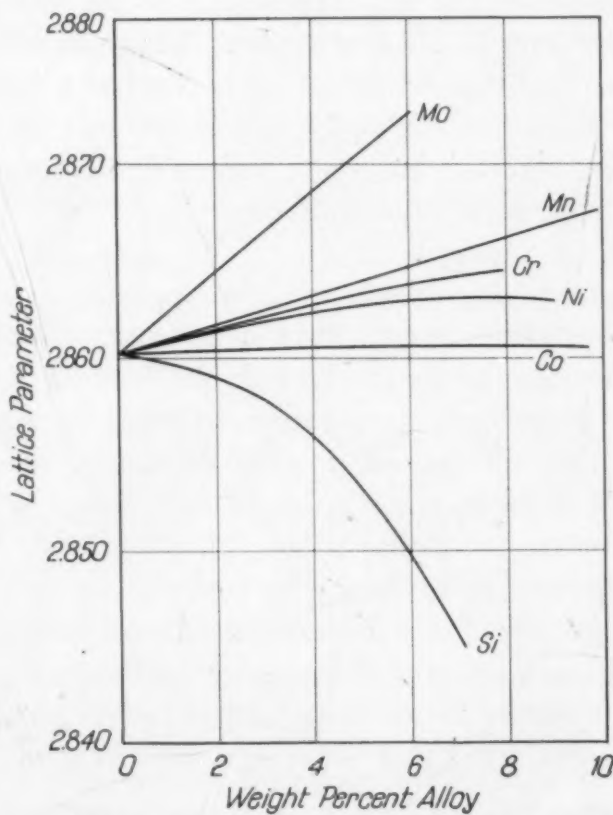


Fig. 6—Data on the Effect of Alloy Additions to the Lattice Parameter of Pure Iron.

Data collected from the literature, on various properties of alloying elements discussed, and on their relation to iron have been included in Table V. The effects of these elements on the lattice parameter of iron as a function of weight per cent added element have been shown in Fig. 6. The relationship in terms of atomic per cent addition is essentially the same.

Cobalt has little effect on the iron lattice and exhibits only minor solid solution hardening. Silicon which has a strong hardening effect on slow cooling is the only element studied which causes a shrinkage in the parameter of the solvent iron. A listing of the elements in order of increasing potency at higher concentrations on change in lattice parameter of iron gives the following order: Cobalt, nickel, chromium, manganese, molybdenum and silicon.

It is to be noted that only chromium has changed position in the list of elements given on page 331 showing the order of increasing potency of hardening, in the fully annealed alloys.

Hume-Rothery (12), in the development of his concepts on solid solubility, points out the restrictions due to the atomic size factor and crystal structure of solute element. Thus chromium which has the body-centered lattice of iron (Table V) has a limited effect on solid solution hardening. Molybdenum, which has the body-centered cubic lattice but exhibits an atomic radius markedly different from ferrite, is a strong solid solution hardener.

In terms of percentage solubility in alpha iron, the elements showing lower solubility produce greater hardening.

These observations permit the following general conclusions:

1. A distortion of the lattice parameter of ferritic iron, either by heating to an elevated temperature followed by rapid cooling or by adding an alloying element in solid solution to effect lattice distortion, results in an increase in hardness. The greater the distortion the greater the hardening effect. This conforms with the generally accepted views on hardening by lattice distortion.
2. The greater the difference in atomic radius between the added element and alpha iron, the greater the hardening effect.
3. The addition of an element possessing a type of crystal structure different from that of iron results in greater solid solution hardening.
4. The addition of elements having low solubility in alpha iron have greater hardening power than those with high solubility.

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DISCUSSION

Written Discussion: By T. D. Yensen, Research Laboratories, Westinghouse Electric & Manufacturing Co., E. Pittsburgh, Pa.

It may be of interest to add a little to the data presented by Professor Austin. In some of my early investigations on vacuum melted iron,¹ tensile tests were made after various heat treatments with the following results (averages for some 15 samples):

Heat Treatment	Stress at Yield Point Psi.	Ultimate Stress Psi.	Elongation Per Cent	Reduction of Area Per Cent
As forged	48,390	54,800	33.3	83
Annealed at 900 degrees Cent. Cooled uniformly in 12 hours	17,960	38,100	51.8	87.4
Annealed at 900 Degrees Cent. Cooled in 24 hours	16,100	35,500	48.6	78.4
Quenched in brine from 1000 degrees Cent.	36,280	50,170	42.5	82.4

This indicated that the ductility as measured by elongation and reduction of area is not greatly affected by the heat treatment, while the strength is, similarly to what Professor Austin finds in regard to hardness.

In regard to the effect of silicon on iron, I found in the investigation referred to by the author that silicon up to 4.5 per cent increases the strength of iron in proportion to the amount added, while the ductility remains almost

¹University of Illinois Engineering Experiment Station Bulletin No. 72, p. 29, 1914.

constant up to 2.5 per cent silicon and becomes nil at 5 per cent silicon. Here again the hardness, as obtained by the author, goes hand in hand with the strength as obtained by myself.

Professor Austin's general conclusion that hardening is related to lattice distortion, and that this in turn is due to difference in atomic size of the elements involved and/or difference in their crystal structure sounds reasonable and seems to be borne out by the evidence presented. It is the same conclusion we have arrived at in regard to lattice distortion and magnetic properties. From this can we now draw the further conclusion that there is a direct relationship between mechanical hardness and magnetic hardness such as coercive force? From Fig. 4 in Professor Austin's paper we see that silicon increases the mechanical hardness of iron more than any of the other elements used. On the other hand silicon may actually decrease the magnetic hardness of iron. If we take Armco iron for example and add 3 to 4 per cent silicon to it and give test pieces from each identical heat treatment, the chances are 10 to 1 that the silicon-iron will have much lower coercive force than the Armco iron. One might argue, however, that Armco iron is contaminated by oxygen which the silicon removes, and that oxygen has an even greater magnetic hardening effect on iron than does silicon. That this may be a good argument is shown by the fact that by removing all impurities from iron down to 1/1000 per cent or less, including oxygen, it is possible to obtain as low or lower coercive force than with silicon-iron of similar purity. In other words, if we should use highly purified iron as the standard instead of commercially pure iron we might arrive at general conclusions in regard to magnetic hardness similar to those arrived at by Professor Austin for mechanical hardness. But one thing is certain, and that is that the curves would not be similar, no matter what is said or done, the sensitivity of iron to other elements is very different in regard to magnetic hardness and mechanical hardness. One hundredth of 1 per cent of carbon or oxygen has no noticeable effect on the mechanical hardness of iron whereas such small amounts affect the magnetic properties tremendously.

Written Discussion: By John R. Low, Jr., instructor, Department of Metallurgy, The Pennsylvania State College, State College, Pa.

In view of the fact that several investigators^{2, 3, 4, 5} have reported notable increases in hardness as a result of quenching and aging in commercial irons containing amounts of carbon similar to those reported by the author for his binary alloys, it would be of interest to know the length of time which elapsed between the heat treatments described and the hardness tests. This is particularly true of treatments III and V which involved water quenching from 650 and 975 degrees Cent. (1200 and 1790 degrees Fahr.) respectively. As an ex-

²J. H. Andrew and E. M. Trent, "The Quench Aging of Steel," *Journal, Iron and Steel Institute*, 1938, II, p. 241.

³J. L. Burns, "The Classification of Alpha Iron-Nitrogen and Alpha-Iron Carbon as Age-Hardening Alloys," *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 113, 1938, p. 242.

⁴A. A. Bates, "Aging in Low Carbon Steels," *TRANSACTIONS, American Society for Metals*, Vol. 19, 1932, p. 454.

⁵G. Masing, "Age-Hardenable Heavy Metal Alloys," *Z. Metallkunde*, Vol. 22, 1930, p. 93.

treme example, Masing and Koch⁵ found that the hardness of a 0.028 per cent carbon steel could be increased from about 90 BHN up to about 160 BHN by quenching from above 600 degrees Cent. (1110 degrees Fahr.) and aging at room temperature for 15 days.

The unexpected softening effect of the initial additions of chromium has also been reported by Edwards, Phillips, and Jones.⁶ These authors made up a series of chromium alloys using Armco iron as a base and found that with increasing chromium, the tensile strength in the annealed state was first lowered and then raised, the minimum occurring at about 1 per cent chromium. The yield point was lowered progressively with increasing chromium, finally disappearing at about 6 per cent chromium. Hardness values were not reported, but it is generally accepted that changes in the yield value and the tensile strength are reflected in similar changes in the indentation hardness. On the basis of this result and similar results with other carbide-forming alloy additions such as titanium, columbium and vanadium, Edwards, Phillips and Jones conclude that the lowering of the yield point comes about as a result of the formation of a "stable" or insoluble carbide which removes the carbon from solid solution. Some such explanation might be put forward to account for the softening effect of chromium reported in the present paper and might also explain the failure of chromium to obey the author's second conclusion that: "The greater the difference in atomic radius between the added element and alpha iron, the greater the hardening effect."

Oral Discussion

A. R. TROIANO:⁷ I feel that the interpretation of solid solution hardening of the common alloying elements (of steel) in iron is, at present, a dangerous procedure. At least two factors contribute to this: first, the limits of solubility, with one or two exceptions, are not well known and in most cases subject to considerable doubt, and, second, the possibility of the martensite type of transformation existing in these systems is very great. The case for a martensite type of transformation in the iron-manganese system has been presented by Troiano and McGuire.⁸

It should be pointed out that no evidence exists which limits the martensite type of transformations to supersaturated solid solutions. Thus the chance of at least some of the observations made here being explained by a martensite type of transformation is quite good. Such a picture would not be inconsistent with the lattice strain-hardness concept. I should like to know if Dr. Austin has given this any consideration.

In the past I have had occasion to make precise lattice constant determinations on quenched as well as annealed high-purity iron and also ingot iron. The lattice constants of both the annealed and quenched iron in each case did not

⁵C. A. Edwards, D. L. Phillips and H. N. Jones, "The Influence of Some Special Elements Upon the Strain-Aging and Yield-Point Characteristics of Low-Carbon Steels," *Journal, Iron and Steel Institute*, 1940, II, p. 203.

⁷Associate professor of metallurgy, University of Notre Dame, Notre Dame, Ind.

⁸A. R. Troiano and F. T. McGuire, "A Study of the Iron-Rich Iron-Manganese Alloys," *TRANSACTIONS, American Society for Metals*, Vol. 31, 1943, p. 340.

vary by more than one part in 50,000 (the estimated accuracy of the determinations). I feel that the hypothesis of the retention of the high temperature parameter characteristics is also dangerous. Indeed if this were true, then the standard X-ray diffraction method for the determination of phase diagrams by quenching powders, etc., would be worthless.

As Dr. Austin has pointed out, surprisingly little is known about solid solution hardening and reaction to heat treatment of iron binary solid solutions, and it is hoped that Dr. Austin will continue his studies in this most important field.

Author's Closure

It is interesting to have additional data on iron and iron alloys from Dr. Yensen, who has contributed so much of value to the literature on the magnetic properties of iron-base materials, and the author thanks him for his comments. Data are being obtained on the tensile properties of the binary solid solution after thorough annealing, and preliminary work suggests that the hardness of the annealed alloy may not serve as an adequate criterion of the tensile strength. Magnetic hardness is of course much more susceptible to change, dependent on minute differences in amounts of impurities in solid solution, than is mechanical hardness, and this is apparently particularly true for elements which take the interstitial position in the iron lattice.

Two interesting aspects of the investigation were brought up by Mr. Low. As regards the length of elapsed time between the heat treatments and the hardness testing, the time varied from 1 day after quenching from 975 degrees Cent. (1790 degrees Fahr.) to 5 days after quenching from 650 degrees Cent. (1200 degrees Fahr.). However, more recent studies on age hardening of these alloys at room temperature and at 45 degrees Cent. (113 degrees Fahr.), after quenching from 650 degrees Cent. (1200 degrees Fahr.), have shown that the increase in hardness up to 1000 hours for pure iron was less than 20 V.P.N. units. After 5 days the hardness increase was only 9 V.P.N. units.

The cited research of Edwards, Phillips and Jones⁶ seems to have particular relevance to the present paper, although the author is not at present in a position to discuss this phase of the subject. At a later date it is anticipated that tensile data will be available on the alloys and it will be useful to observe what correlation exists between hardness and tensile strength or yield point. For the present it may be noted that the shape of the tensile-per cent chromium curve of Edwards and his co-workers is very similar to the hardness-per cent chromium curve of the present author, but the yield point-composition curve is quite dissimilar. Furthermore, Edwards found that age-hardening, which was presumed to be due to the presence of carbon, can be neutralized by chromium. The author's chromium alloys appeared to be essentially free from quench aging and from strain aging. However, it would be of considerable interest to ascertain definitely if the decrease in hardness of iron on the addition of chromium was purely a solid solution effect or dependent on its influence on impurities.

Dr. Troiano brings up some points requiring comment. So far as the

author is aware, it has been clearly established that all the alloys studied, with the exception of iron manganese, are true solid solutions. The complex nature of the iron-manganese binary alloys, even at low manganese concentration, was pointed out by Walters and his co-workers several years ago and cognizance of this fact has been reported in the paper. In all the other alloys we appear to be concerned with simple phase change-free solid solutions when considering heat treatment below the gamma-alpha inversion and with the lattice change effect alone when cooling from above the critical. The writer prefers to consider this as a Widmanstätten rather than a martensitic structure.

The discussion on possible relation of lattice parameter to hardness measured dealt wholly with alloys cooled rapidly from temperatures below the alpha-gamma inversion and hence apparently free from any complication dependent on possible development of Widmanstätten structures.

Finally we are appreciative of the information on precise lattice constant determinations and fully realize that the hypothesis is open to experimental verification. Studies are continuing on an extended series of iron binary alloys and it is hoped that some X-ray data may also be obtained to permit more clearly defined relations between lattice parameter and mechanical hardening.

A STUDY OF THE IRON-RICH IRON-MANGANESE ALLOYS*

BY ALEXANDER R. TROIANO AND FRANCIS T. MCGUIRE

Abstract

Precision lattice constant determinations correlated with a microscopic investigation have allowed an accurate determination of the alpha and alpha plus gamma phase boundaries of the iron-manganese system. Direct evidence is presented for the existence of two types of alpha solid solutions (equilibrium and supersaturated alpha). The disturbing and sometimes misleading effects of supersaturated solid solutions are discussed and evaluated, with reference to both this and other systems.

The results of deformation and long time annealing studies of the epsilon structure lead to the conclusion that epsilon is not stable. Finally, a high speed thermal analysis coupled with deformation, X-ray, and microscopic observations present evidence that two martensite reactions occur in the iron-rich portion of this system.

THE constitution of the binary alloys of iron and manganese has been the subject of considerable research. Despite this, many of the phase limits are in doubt and the most recent critical compilation of data to present an iron-manganese phase diagram (1)¹ admittedly does not give the boundaries of the alpha and gamma phases at conditions of equilibrium. Several factors have contributed to this. As generally recognized diffusion in these alloys is slow at relatively low temperatures, thus long-time annealing is necessary to attain equilibrium at temperatures near 500 degrees Cent. (930 degrees Fahr.) and below. Another factor not so generally recognized is the existence of two reactions of the martensite type, which characteristically cannot be suppressed by the maximum cooling

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

*Much of the material presented in this paper has been abstracted from a thesis submitted by F. T. McGuire in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Notre Dame, June 1941.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. Of the authors, Alexander R. Troiano is associate professor of metallurgy, University of Notre Dame, Notre Dame, Indiana, and Francis T. McGuire is associate professor of metallurgy, University of Kentucky, Lexington, Kentucky.

velocities obtainable. The complicating effect of this type of reaction will be discussed in connection with the present investigation.

In the range of the iron-rich alloys three structures have been detected and studied. They are: the alpha solid solution, body-centered cubic; the gamma solid solution, face-centered cubic; and the epsilon solid solution, hexagonal close-packed with an axial ratio of approximately 1.605.

The temperature of the gamma \rightleftharpoons alpha transformation, with various rates of slow cooling, has been studied by Rumelin and Fick (2), Gumlich (3), Dejean (4), Ishiwara (5), Esser and Ober-

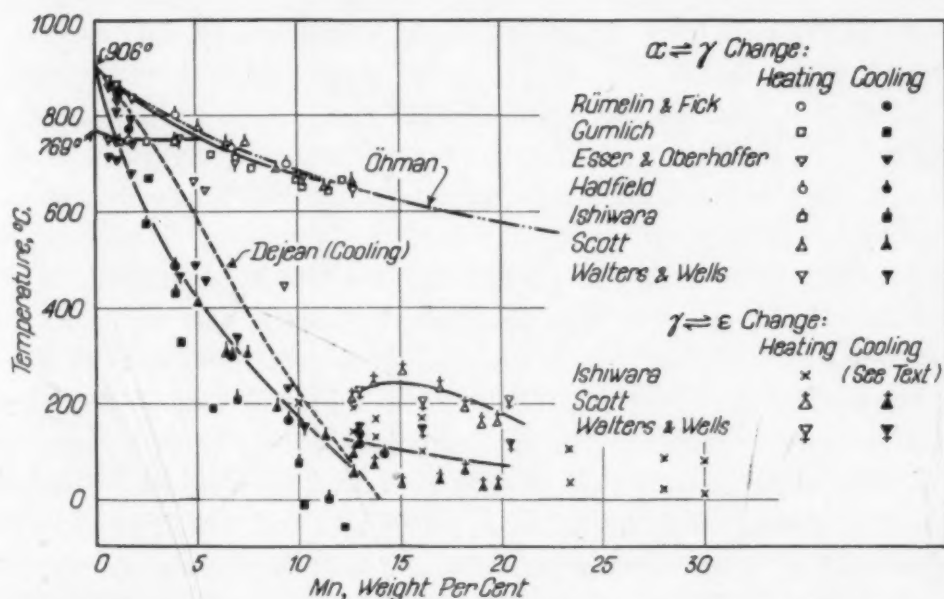


Fig. 1—Summary of Transformation Temperatures in Iron-Rich Iron-Manganese Alloys (Hansen).

hoffer (6), Hadfield (7), Scott (8), and Walters and co-workers (9), (10), (11), (12). This work probably reached its apex in the dilatometric investigations of Walters and co-workers (10), (12) with carefully prepared alloys of high purity. Fig. 1, taken from Hansen's (13) excellent review of the literature, summarizes the results obtained by various investigators on the gamma \rightleftharpoons alpha and also the gamma \rightleftharpoons epsilon transformation. Of particular interest is the hysteresis effect observed by almost all investigators.

The first X-ray diffraction study was performed by Bain (14) who detected the presence of the alpha and gamma solid solutions based on alpha and gamma iron. Schmidt (15) first observed the epsilon structure, determined its crystal structure to be hexagonal

close-packed, and found that the axial ratio was approximately a linear function of the manganese content. In addition he observed that alpha was present in alloys containing 0 to 20 per cent manganese, epsilon from 12 to 29 per cent manganese, and gamma from 16 to 60 per cent manganese. This was closely followed by other X-ray work confirming in general the results of Schmidt. Among the more comprehensive of these later investigations may be mentioned those of Osawa (16), Öhman (17), Gensamer, Eckel and Walters (18), and Walters and Wells (19).

Binary iron-manganese constitutional diagrams have been presented by Öhman (17), Ishiwara (5), Gayler (20), and Walters and Wells (19). Of these investigators only Öhman, as the result of a comprehensive X-ray diffraction study, made any serious attempt to establish the limits of the alpha and gamma phases at conditions approaching equilibrium. Within the limit of accuracy of his technique, Öhman observed that the lattice parameter of the alpha solid solution was not measurably different from that of alpha iron. Hence he concluded that the solubility of manganese in alpha iron was very small.² The alpha plus gamma, gamma phase boundary was established in part by lattice constant measurements. However the boundary in the region of 500 degrees Cent. (930 degrees Fahr.) was placed by inspection only because of the diffuse character of the gamma lines. It is interesting to note that Öhman observed the presence of super-saturated alpha, which he called alpha prime, and which he carefully differentiated from equilibrium alpha. Despite this, many investigators in both this and other analogous systems, such as iron-nickel, have confused these two types of solid solutions and hence arrived at erroneous conclusions. Recently, two abstracts (21), (22) have appeared of work performed by Russian investigators. It is stated that, "in the annealed iron-manganese alloys, the alpha region extends to about 3 per cent manganese and is followed by the alpha plus gamma region up to about 25 per cent manganese, beyond which the homogeneous gamma-solution region exists." No times, temperatures, or other details are given and the original articles are not available at this time.

The nature of the epsilon solid solution has been the subject of

²The results of this investigation show that a change in the lattice parameter of one part in 1000 (Öhman's stated accuracy) indicates a change of approximately 4.5 per cent in the solubility of manganese in the alpha solid solution. Thus it is obvious that in a system such as this only the most precise determinations of the lattice constants will allow the solubility limits to be placed accurately.

much speculation. Schmidt (15) properly observed that the variation of lattice constants of epsilon with varying composition in specimens containing alpha and gamma or gamma, as well as epsilon was in contradiction to the phase rule. He considered the gamma→epsilon transformation to be analogous to the austenite→martensite transformation in steel. Öhman (17), also Bain, Davenport and Waring (23), considered epsilon to be a transition structure of the martensite type. Ishiwara (5) stated that epsilon was an intermetallic compound formed as the result of a peritectoid reaction. Walters and Eckel (24) presented thermomagnetic data which they stated suggested the possibility of the peritectoid reaction alpha plus gamma \rightleftharpoons epsilon. Perhaps the strongest argument against the concept of epsilon as a transition structure to alpha has been the inability of any investigator to cause epsilon to decompose to alpha.

EXPERIMENTAL METHODS

Materials—Electrolytic manganese and iron were employed in the preparation of all alloys. The manganese was obtained from the Electro Manganese Corporation. The manufacturer reported the iron content as 0.03 per cent and sulphur 0.02 per cent with copper, carbon, silicon, aluminum, nickel and cobalt stated as nil. For this investigation the iron is not an impurity and the small amount of sulphur undoubtedly forms insoluble manganese sulphide. The hydrogen-annealed electrolytic iron was obtained from the Westinghouse Research Laboratories. Precision lattice constant measurements showed the iron to be of high purity. Five determinations gave an average value of $a_0 = 2.8607_2 \text{ \AA}$. This is in good agreement with the average value of $a_0 = 2.8607_4 \text{ \AA}$ obtained by Jette and Foote (25) on four specimens of high-purity iron.

All alloys were prepared in high-purity magnesia crucibles made by the Norton Company from their mixture R.M. 998.

Preparation of Alloys—The alloys were melted in a vacuum induction furnace under an atmosphere of purified medical helium. Close inductive coupling compensated for the relatively high thermal conductivity of helium. The crucibles were preheated to 1000 degrees Cent. (1830 degrees Fahr.) and when sufficiently cool to handle were carefully charged in a manner such that a minimum of unalloyed molten manganese came in contact with the crucible.

The melting practice was as follows: The furnace was evacuated

to a pressure of less than 10^{-3} mm. mercury, then helium was admitted until atmospheric pressure was again obtained. This procedure was repeated a minimum of five times. The charge was then very slowly heated under a pressure of 10^{-3} mm. mercury until a dull red glow was observed. Finally the charge was melted with helium maintained at atmospheric pressure. The ingots weighed approximately 200 grams and all showed a clean bright metallic surface.

Following this all ingots were hot-forged at 1000 degrees Cent. (1830 degrees Fahr.) into approximately $\frac{3}{8}$ -inch square bars, which were subsequently homogenized in a vertical tube furnace wound

Table I*
Chemical Analyses

Alloy	Weight Per Cent Manganese
A 0.5	0.46
A 1	1.15
A 2	2.14
A 2.5	2.37
A 3	3.18
A 4	4.09
A 5	5.72
A 10	10.62
A 13	13.00
A 15	15.24
A 17	16.74
A 20	20.23
A 25	26.20
A 30	30.09
A 40	39.33
A 50	50.02

* All analyses were performed by Walter M. Saunders, Analytical and Consulting Chemist, Providence, Rhode Island.

All compositions are by weight per cent except where specifically noted otherwise. It should be remembered that the atomic weight of manganese differs only slightly from that of iron causing the atomic and weight per cents of a given alloy to be nearly the same.

with platinum-rhodium wire and fitted with a special alundum inner sleeve. The bars were suspended freely inside the sleeve in a slightly positive pressure of helium. All bars were held from 18 to 36 hours at 10 to 20 degrees Cent. below the temperature of the solidus. Subsequent microscopic and X-ray diffraction examination demonstrated that this treatment was adequate to insure homogenization.

Chemical Analysis—The homogenized bars were analyzed for iron, manganese and carbon.* The analyses are given in Table I. The carbon content of all alloys was stated by the analyst to be less than 0.005 per cent carbon.

Preparation of Specimens—The specimens were prepared from the homogenized bars after removing an outer skin of 0.03 to 0.04 inch. Powders were prepared by filing and slivers approximately

1 by 1 by 10 mm. were cut with a jeweler's saw. A sliver and powder of the same alloy were placed in small glass tubes which were evacuated to a pressure of less than 10^{-3} mm. mercury, then successively flushed with helium and evacuated a minimum of five times. Before sealing, a residual helium pressure was left in the tubes calculated to be equal to atmospheric pressure at the temperature of the individual treatment. This minimized loss of manganese by vaporization. For temperatures below 600 degrees Cent. (1110 degrees Fahr.) Pyrex glass tubing was used; at 600 degrees Cent. and above clear fused quartz was satisfactory.

All specimens were held at specified temperatures which did not deviate by more than ± 2 degrees Cent. from the temperature setting. This was accomplished by the use of automatic pyrometer controls wired so as to by-pass the major portion of the heating current.

Methods of Analysis—All samples, both powders and slivers, were examined by X-ray diffraction methods. Debye patterns were taken with the characteristic K-alpha radiation of chromium to study the nature of the phases present. Precision lattice constants were determined by use of a back-reflection focusing camera combined with Cohen's (26) method of calculating the parameters, corrected for systematic errors.

Alloy targets were employed in order to obtain a favorable distribution of reflections over the relatively limited angular range of this type of camera. For determination of the alpha phase parameters, the characteristic K-alpha radiations of chromium, iron and cobalt were used. The possibilities of proper radiations for the gamma phase are rather limited, but a chromium and manganese alloy target gave adequate results.³ The accuracy of the alpha phase parameter determinations are believed to be approximately one part in 50,000 and that of the gamma phase slightly better than one part in 30,000.

All specimens were quenched very rapidly into water with the glass tubes almost immediately broken under the water. The specimens were then quickly rinsed with alcohol a minimum of three times and dried in warm air. No samples were used that did not exhibit a bright metallic luster following this treatment.

Microscopic examination of the slivers allowed a direct correla-

³A vanadium target used in conjunction with the chromium-manganese target gave an additional set of reflections but the increase in the ratio of background to line intensity did not justify its extensive use. Had it been necessary this objectionable feature could have been minimized by evacuating the camera.

tion between X-ray diffraction observations and microstructure. The best etching reagents were found to be 2 per cent nital and 4 per cent picral. Extensive use of darkfield illumination proved to be advantageous particularly for specimens which contained supersaturated alpha.

In addition to the above, a thermal analysis of the gamma \rightleftharpoons alpha and gamma \rightleftharpoons epsilon transformation was made. A small helium gas-quenching furnace coupled with a low-period torsion galvanometer and a drum camera allowed high velocity thermal analyses to be made. This equipment was designed and has been described by Greninger (27). Small specimens approximately 0.04 inch square and 0.015 inch thick allowed cooling velocities in excess of 9000 degrees Cent. per second to be attained. The specimens were supported in the gas-quenching furnace by means of 40 gage chromel-alumel thermocouples, spot welded to the specimens.

EXPERIMENTAL RESULTS

Equilibrium Studies—All specimens employed for the equilibrium studies were held at the various temperatures for the following approximate times: 300 degrees Cent. 720 days; 400 degrees Cent. 545 days; 500 degrees Cent. 520 days; 600 degrees Cent. 90 days; 700 degrees Cent. 10 days; 800 degrees Cent. 1 day; 900 degrees Cent. 1 hour. In addition several specimens were annealed at 550 degrees Cent. for 60 days. Because of the anticipated long annealing times, specimens at 600 degrees Cent. and below were placed at each temperature in triplicate.

With the exception of 300 degrees Cent. and below, the above annealing times were sufficient to attain equilibrium. At 300 degrees Cent. and below, 2 years were not sufficient to attain equilibrium, although some alloys exhibited a marked improvement in the sharpness of the X-ray diffraction lines, indicating that equilibrium was being approached.

Only certain strategic compositions and temperatures gave diffraction lines of sufficient sharpness to allow the previously stated precision of lattice parameter determinations. At other compositions and temperatures, the gamma phase transformed on quenching to either supersaturated alpha or epsilon with a consequent production of diffuse reflections. The formation of supersaturated alpha from gamma usually effectively masked any equilibrium alpha that may

have formed at the annealing temperature, and in those cases where gamma was retained with supersaturated alpha, the gamma lattice was distorted causing its reflections to be diffuse also. The formation of epsilon had the same effect on the gamma lattice.

Thus it becomes obvious that the formation of supersaturated alpha and epsilon imposed very definite limitations upon the placement of the phase boundaries by precise determination of lattice constants as obtained after quenching to room temperature. Only those specimens which gave results pertinent to the conclusions drawn in this investigation will be discussed. The specimens which yielded results useful in determining the alpha and gamma phase boundaries are listed in Tables II to V inclusive, together with the lattice constants,⁴ temperatures, and times.

Table II
Alpha Field

Spec. No.	Atomic Per Cent Manganese	a_0 Å
A 0.5	0.47	2.8608 ₆
A 1	1.17	2.8610 ₉
A 2	2.17	2.8617 ₀
A 2.5	2.41	2.8618 ₃
A 3	3.25	2.8623 ₅

Table III
Alpha and Gamma Field

Spec. No.	Atomic Per Cent Manganese	Temp. °C.	Time, Days	a_0 Å
A 4	4.09	400	544	2.8623 ₂
A 4	4.09	500	520	2.8624 ₂
A 3	3.25	600	90	2.8621 ₈
A 3	3.25	700	10	2.8621 ₀
A 3	3.25	800	4	2.8614 ₄

It is significant that compositions in the alpha plus gamma field which yielded diffraction lines that allowed precise determinations of lattice constants of alpha were close to the alpha phase boundary. For these compositions, only small amounts of gamma existed at the annealing temperature to form supersaturated alpha on quenching and thus did not produce enough supersaturated alpha to mask effectively or disturb the equilibrium alpha.

The results listed in Tables II to V inclusive allowed the alpha and gamma phase boundaries to be accurately placed as shown in Fig. 2. The course of the gamma boundary above 600 degrees Cent. (1110 degrees Fahr.) is not placed with the same degree of accuracy

⁴All lattice constants corrected to 25 degrees Cent.

Table IV
Gamma Field

Spec. No.	Atomic Per Cent Manganese	a_0 Å
A 13	13.19	3.5807
A 15	15.45	3.5838
A 17	16.97	3.5854
A 20	20.50	3.5882
A 25	26.52	3.5953
A 30	30.44	3.6004
A 40	39.72	3.6114
A 50	50.43	3.6237

Table V
Alpha and Gamma Field

Spec. No.	Atomic Per Cent Manganese	Temp. °C.	Time, Days	a_0 Å
A 25	26.52	400	540	3.5961
A 20	20.50	500	520	3.5890
A 15	15.45	550	60	3.5857
A 13	13.19	600	90	3.5817

as the other portions. However visual examination of the character of the microstructure and the Debye patterns allowed it to be placed with greater accuracy than that obtainable by a mere extrapolation.

Non-Equilibrium Results—Significant results other than those employed in the determination of the phase diagram can be presented best in terms of the newly established diagram of Fig. 2.

The slivers required longer annealing times to reach equilibrium, although the maximum times employed were sufficient to attain equilibrium. This same effect has been observed in other systems, for example the work of Bradley and Goldschmidt (28) on the iron-nickel system. This is probably the result of the greater amount of cold work which the powders received.

At all temperatures, the X-ray diffraction lines obtained from specimens quenched from the homogeneous alpha phase field were very sharp. In addition all specimens annealed at 400 degrees Cent. (750 degrees Fahr.) gave sharp lines of alpha and gamma. Thus, from Fig. 2, we see that gamma of approximately 27.5, or more atomic per cent manganese does not transform to either super-saturated alpha or epsilon. Specimens of A 50 at 400, 500, and 600 degrees Cent. (750, 930, and 1110 degrees Fahr.) exhibited strong lines of the alpha-manganese solid solution; but above 600 degrees Cent. (1110 degrees Fahr.) only gamma was observed. The presence of alpha manganese in A 50 was unexpected. Only Öhman's early

investigation indicated this condition and more recent work has placed the gamma, gamma plus alpha-manganese boundary above 50 per cent manganese.⁵

For all temperatures gamma of approximately 3 to 15 atomic per cent manganese gave lines of supersaturated alpha. The amount of supersaturated alpha increased with the amount of gamma present. This supersaturated alpha was characterized by diffuse lines displaced

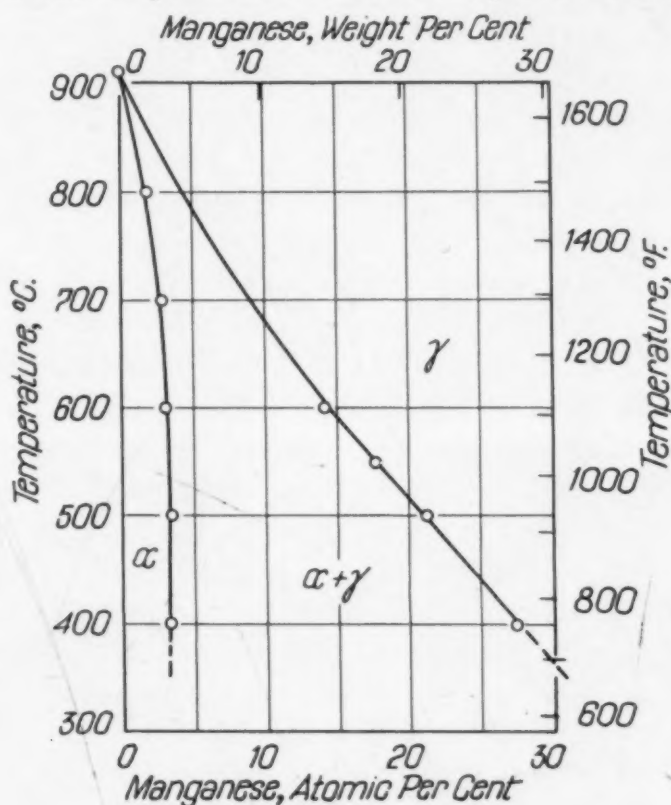


Fig. 2—Determination of the Alpha and Alpha Plus Gamma Phase Boundaries.

so as to indicate an abnormally large lattice parameter. In this connection several combinations of temperature and composition in the alpha plus gamma field yielded interesting results. For example, according to Fig. 2, alloy A 5 at 700 degrees Cent. (1290 degrees Fahr.) forms approximately 40 per cent equilibrium alpha containing 2.5 per cent manganese and 60 per cent equilibrium gamma of 8.4 per cent manganese. On quenching to room temperature the gamma transformed to supersaturated alpha of the same composition. The X-ray diffraction patterns definitely indicated the presence of the two alpha solid solutions; namely, equilibrium alpha with sharp lines

⁵The phase diagram from 50 to 100 per cent manganese is under investigation at the present time. The results are expected to be ready for publication soon.

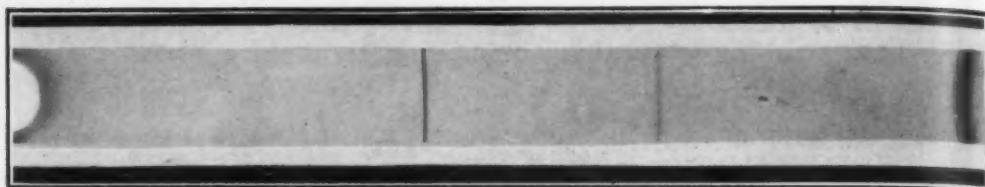


Fig. 3—Debye Pattern of Sliver of Alloy A 5, Annealed 10 Days at 700 Degrees Cent. The $\{211\}$ Lines Exhibit the Presence of the Equilibrium and Supersaturated Alpha Solid Solutions.

and supersaturated alpha with diffuse lines displaced at smaller values of the Bragg angle. Fig. 3 shows a Debye pattern, taken with chromium radiation, of a sliver of alloy A 5, held at 700 degrees Cent. (1290 degrees Fahr.) for 10 days and quenched into H_2O . The $\{211\}$ lines (near back-reflection) clearly demonstrate the existence of the two types of alpha. Note the diffuse line of supersaturated alpha displaced at a smaller value of the Bragg angle (larger lattice constant) than the resolvable doublet of equilibrium alpha.

Gamma of approximately 13 to 20 per cent manganese formed epsilon. These results were slightly modified by two variables other than composition which obviously affected the formation of epsilon. They were quenching temperature and specimen size. In general, the higher the quenching temperature and the larger the specimen the greater was the amount of epsilon produced. However in no case with any quenching temperature and specimen size was epsilon observed below approximately 10 and above 26 per cent manganese.

Microscopic Study—All microscopic observations were made on slivers which had been previously analyzed by X-ray diffraction methods. The microstructures observed were much the same as those published by other investigators (20), (29). Specimens at equilibrium quenched from the alpha field exhibited the usual polygonal grains characteristic of a homogeneous solid solution. Specimens in which the X-ray analysis indicated the presence of supersaturated alpha exhibited all the microstructural characteristics of low-carbon martensite in steel. And where the X-rays indicated the presence of epsilon the multiple twin-like structure illustrated by other investigators was observed.⁶

However, the microstructure of specimens located, with respect to composition and temperature, so as to give two alpha solid solutions (normal equilibrium alpha and the supersaturated alpha) exhibited interesting and corroborative features. Figs. 4a and 4b illus-

⁶For good photomicrographs of epsilon see, particularly, Wells and Walters (30), and Wohrman (31).

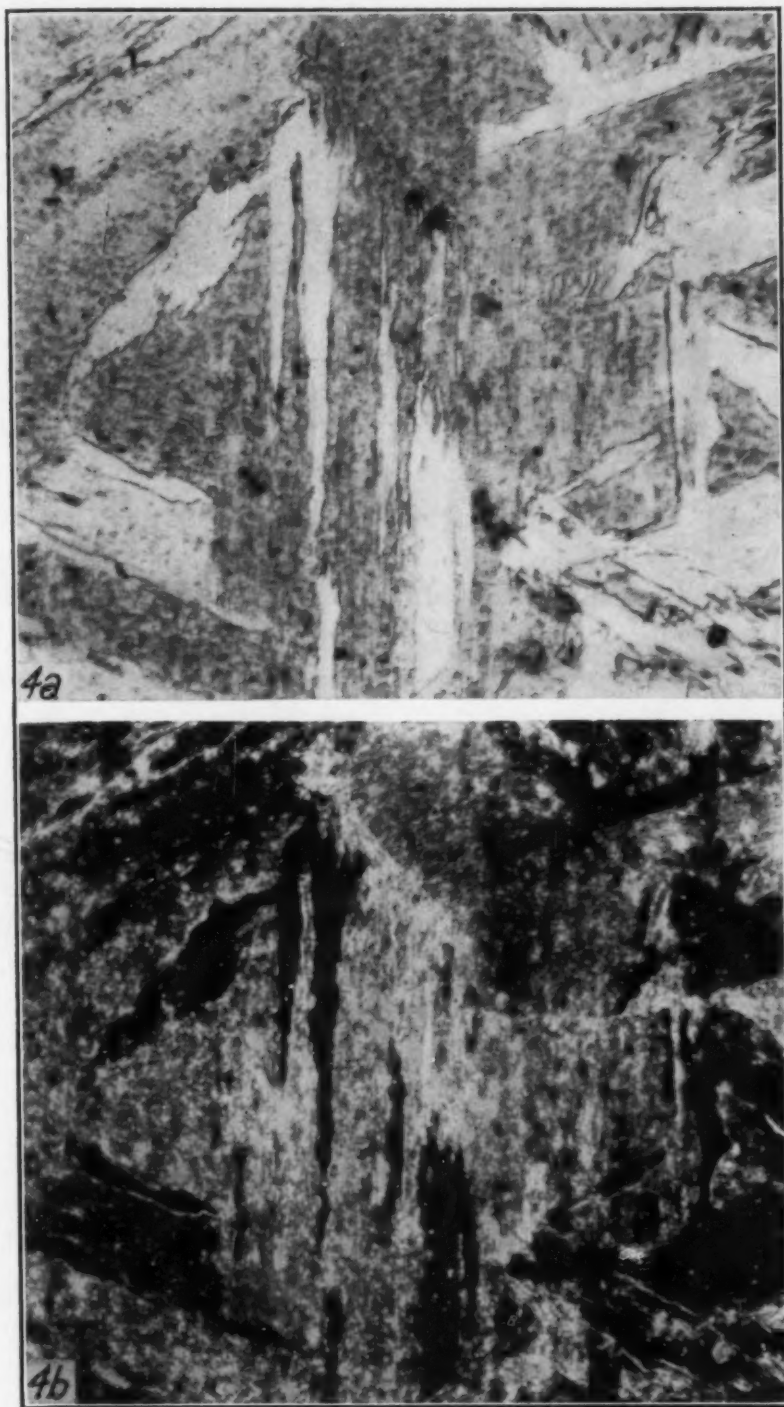


Fig. 4—Microstructure of the Same Sliver as that of Fig. 3. Illustrating the Appearance of Equilibrium and Supersaturated Alpha. $\times 500$.

a.—Etched with 2 Per Cent Nital. Light Constituent is Equilibrium Alpha and Matrix is Supersaturated Alpha.

b.—Same Area as in Fig. 4a Only Darkfield Illumination.

trate the microstructure of the same sliver of A 5 as the one whose Debye pattern is shown in Fig. 3. In Fig. 4a the light precipitate is equilibrium alpha and the matrix supersaturated alpha. Fig. 4b shows the same area as in Fig. 4a but with darkfield illumination. The contrast between the two alpha solid solutions is more striking than with brightfield illumination.

Epsilon Study—Because of the speculative nature of the present concepts of the epsilon structure, an attempt was made to analyze any decomposition of epsilon that might occur below the temperature of the epsilon \rightarrow gamma transformation. Accordingly, both powders and slivers of A 10, A 13, A 15, A 17, and A 20 were quenched from the gamma phase field and subsequently cold-worked and X-rayed. The cold work was performed in approximately five stages with Debye patterns taken after each stage. The retained gamma in A 10 and A 13 transformed almost entirely to supersaturated alpha with a slight trace of epsilon. Slivers of A 15 and A 17 provided the most significant results. After quenching, the Debye patterns indicated the presence of approximately equal amounts of gamma and epsilon with no alpha. At intermediate stages of deformation (approximately 40 to 60 per cent reduction in area) almost all epsilon with a small amount of supersaturated alpha was present. It was not possible to determine whether this alpha formed as the result of the decomposition of either gamma or epsilon or possibly both. However, after severe deformation the Debye patterns indicated the presence of almost all supersaturated alpha with a trace of epsilon. This large amount of additional supersaturated alpha could have formed only by the decomposition of epsilon.

Following this, all deformed specimens including slivers of A 15 and A 17 with moderate deformation were placed in reflux condensers and annealed at 100 degrees Cent. (water), 150 degrees Cent. (methyl n-amyl ketone) and 200 degrees Cent. (carbitol) for times varying from one and one-half to two years. According to Fig. 5 these temperatures are below the beginning of the epsilon \rightarrow gamma transformation temperature.⁷ Thus any decrease in the amount of epsilon must be the result of the direct decomposition of epsilon. All specimens in the 200-degree Cent. bath definitely indicated that composition readjustments necessary to form equilibrium alpha and gamma were taking place. The sliver of A 15, moderately deformed and

⁷Specimens of A 20 at 200 degrees Cent. were not included.

held at 200 degrees Cent. for 718 days, showed this in convincing fashion. Originally it contained a large amount of epsilon but after annealing only alpha was present. Although the alpha lines were not sharp enough to allow accurate lattice constant determinations, their position had shifted almost to that required by equilibrium alpha. Lines of the gamma phase normally expected as the result of composition readjustments to attain equilibrium were not observed. This same phenomenon was observed in the equilibrium study at 300 de-

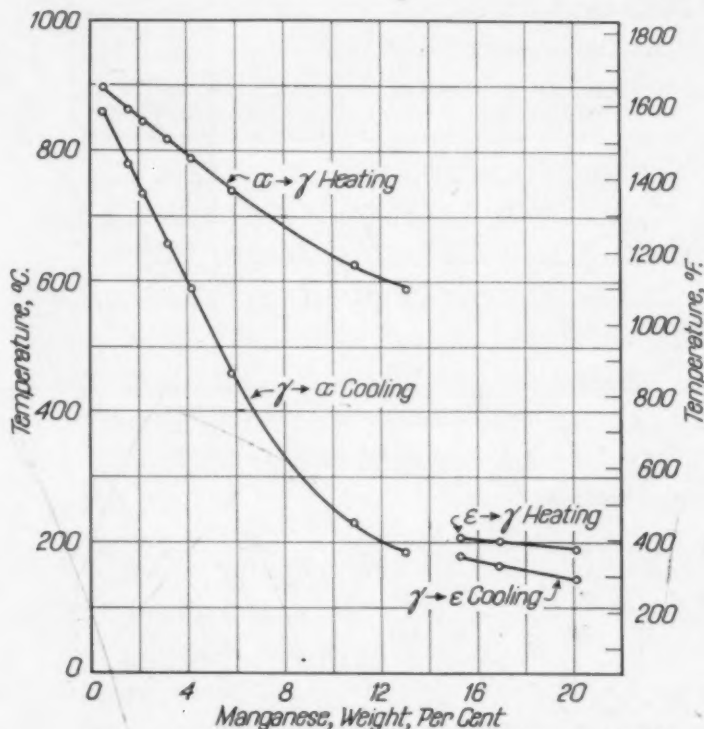


Fig. 5—Initial Transformation Temperatures for the Gamma \rightleftharpoons Alpha and Gamma \rightleftharpoons Epsilon Transformations.

grees Cent. and also by Owen and Sully (32) in analogous alloys of iron and nickel. This may be the result of a particle size effect since gamma must precipitate from a matrix of either supersaturated alpha, or epsilon, or both. Microscopic examination offered no evidence to disprove this hypothesis.

Thermal Analysis—All specimens employed in the thermal analysis were heated in the gas-quenching furnace a minimum of 15 minutes at 990 to 1000 degrees Cent. (1815 to 1830 degrees Fahr.) in an atmosphere of purified helium. Fifteen minutes was adequate for complete solution as demonstrated by the fact that the results were the same for specimens occasionally held for longer times. Cooling velocities of approximately 450, 3000 and 9000 degrees Cent.

(840, 5430 and 16,230 degrees Fahr.) per second measured at 900 degrees Cent. (1650 degrees Fahr.), and a heating velocity of approximately 600 degrees Cent. (1110 degrees Fahr.) per second measured at 150 degrees Cent. (300 degrees Fahr.) were employed in the examination of all specimens. At least 3 curves were taken on two specimens of each composition for each individual cooling or heating velocity.

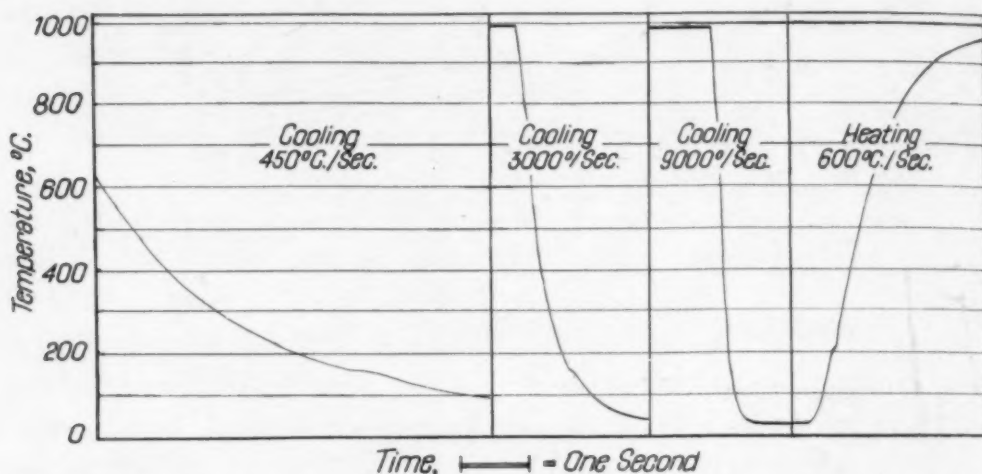


Fig. 6—Typical Set of Cooling and Heating Curves for Alloy A 17. Note the Independence of Cooling Velocity with Temperature of Initial Transformation, and the Hysteresis Effect on Heating.

The results of these tests for a cooling velocity of 450 degrees Cent. (840 degrees Fahr.) per second and heating velocity of 600 degrees Cent. (1110 degrees Fahr.) per second have been used to construct Fig. 5. For all specimens containing more than 3.2 per cent manganese the temperature of the beginning of both the gamma \rightarrow alpha and the gamma \rightarrow epsilon transformations was independent of cooling velocity. In the low-manganese specimens increased cooling velocities slightly depressed the temperature of the gamma \rightarrow alpha transformation, with the effect a maximum in the specimen containing the least manganese (A 0.5). No further quantitative analysis of this effect was made, but it is interesting to note that the same phenomenon exists in pure iron. The independence of temperature of beginning of transformation with cooling velocity is a definite characteristic of a martensite transformation. Fig. 6 shows a typical set of curves for a complete thermal analysis of the gamma \rightleftharpoons epsilon transformation in A 17. The independence of initial transformation temperature with cooling velocity and the hysteresis effect on heating are both plainly indicated.

CONCLUSIONS

Fig. 2 shows the limits of the alpha and alpha plus gamma phase fields determined with a high degree of accuracy. The solubility limits obtained as a result of this investigation indicate changes of more than 10 per cent manganese in some portions of Öhman's diagram. There is a striking similarity between the shape of the alpha and alpha plus gamma solubility limits presented here and the corresponding limits for the iron-nickel system presented by Owen and Sully (32). This is not unusual considering the many characteristics that manganese and nickel possess in common, especially with respect to their effect on steel.

The presence of supersaturated alpha, the formation of which could not be suppressed by the maximum cooling velocities obtained, introduced interesting complicating factors. X-ray reflections of supersaturated alpha are always diffuse and hence have led some investigators to confuse this condition with the diffuse lines caused by heterogeneity as the result of insufficient annealing. Obviously no amount of annealing will eliminate the diffuse lines of supersaturated alpha because equilibrium gamma within definite composition limits will transform, in part at least, to supersaturated alpha regardless of the cooling velocity. Thus, a specimen annealed in the two-phase field to obtain equilibrium alpha and equilibrium gamma, and in which this gamma is of the proper composition to transform to supersaturated alpha, should exhibit the presence of both the equilibrium and supersaturated alpha solid solutions. Figs. 3 and 4 offer conclusive evidence of the existence of the two alpha solid solutions and, in addition, clearly demonstrate the corroborative evidence obtained by directly correlating X-ray and microscopic observations.

Martensite transformations have been observed in many systems and undoubtedly exist in many others where they have not yet been detected. Little imagination is necessary to conceive of the confusion that may occur in an equilibrium study of a multi-component system in which one or more martensite transformations occur without the investigator's appreciation of their full effect. It would be particularly confusing where the crystal structure of the product of the martensite reaction is the same as an equilibrium phase in a nearby portion of the diagram.

It was possible to decompose epsilon to form supersaturated alpha at room temperature by means of deformation. In addition,

long time annealing below the temperature of the epsilon \rightarrow gamma transformation caused epsilon to decompose and alpha to approach equilibrium. These results can lead only to the conclusion that, although epsilon is very persistent, it is not a stable phase, and hence has no place on the phase diagram.

The results of the high speed thermal analysis confirm the general features of previous work on the gamma \rightleftharpoons alpha and gamma \rightleftharpoons epsilon transformations and extend the study from cooling and heating velocities of approximately 10 degrees Cent. per minute to cooling velocities of 9000 degrees Cent. (16,230 degrees Fahr.) per second and a heating velocity of 600 degrees Cent. per second. The temperature of the gamma \rightarrow supersaturated alpha and gamma \rightarrow epsilon transformations are independent of the cooling velocity.

The alpha plus gamma, gamma phase boundary shown in Fig. 2 lies remarkably close to the alpha \rightarrow gamma heating curve of Fig. 5. All heating curves were taken after quenching from 990 to 1000 degrees Cent. (1815 to 1830 degrees Fahr.) and hence contained alpha (supersaturated above approximately 3 per cent manganese) of the same composition as the gamma from which it formed. Thus, the alpha \rightarrow gamma transformation on heating did not involve any composition readjustments but only a crystal structure change. On this basis, the lack of superheating is not surprising because superheating and supercooling in alloy systems are associated with composition changes necessary for equilibrium. A comparison of the alpha plus gamma, gamma boundary of Owen and Sully (32) for the iron-nickel system, with the alpha \rightarrow gamma heating curves of Honda and Miura (33) for the same system, shows fair agreement. The major portion of the alpha plus gamma, gamma phase boundary lies between the beginning and end of the alpha \rightarrow gamma transformation temperatures on heating. Honda and Miura state that their curves were taken at "very slow" heating rates; thus it is highly probable that a faster heating rate would yield results showing better agreement for the iron-nickel system. In fact, the deviations from actual agreement are such as to indicate strongly that this is true. This correlation between heating curves and phase boundaries suggests interesting possibilities for a simple and quick method of obtaining analogous phase limits with reasonable accuracy in multi-component systems which exhibit supersaturated solid solutions.

It is concluded that supersaturated alpha and epsilon are the

products of a martensite type of reaction. That is, they form by a shear mechanism, without diffusion, and are not stable phases. Both supersaturated alpha and epsilon exhibit all the typical characteristics of iron-carbon martensite. The lattice constants of both structures are linear functions of composition in what appear to be two- or three-phase fields. The phase rule does not allow this situation for equilibrium phases but does not rule out unstable structures. The microstructures are analogous to those found in iron-carbon martensite, especially those of supersaturated alpha. Deformation of persistent gamma will produce either or both structures and, finally, the initial temperature of formation of either structure cannot be depressed by the maximum cooling velocities obtainable. These results indicate that epsilon as well as supersaturated alpha are martensite (transition) structures. Indeed, it is an untenable hypothesis to believe that epsilon forms as the result of a peritectoid reaction. The peritectoid reaction involves the reaction of two solid phases to produce a third new solid phase and is necessarily very slow. Thus it is inconceivable that such a reaction could occur at temperatures near 200 degrees Cent. (390 degrees Fahr.) and at cooling velocities of 6000 degrees Cent. (11,430 degrees Fahr.) per second,⁸ especially in this system where two years at 300 degrees Cent. (570 degrees Fahr.) was not sufficient time to attain equilibrium.

ACKNOWLEDGMENTS

The authors wish to express their appreciation of the advice and continued interest of Professor E. G. Mahin, Head, Department of Metallurgy, University of Notre Dame. The donation of the electrolytic manganese by Mr. K. M. Leute, President, The Electro Manganese Corporation, is gratefully acknowledged.

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⁸6000 degrees Cent. (11,430 degrees Fahr.) per second is the approximate maximum cooling velocity at the temperature of the gamma \rightarrow epsilon transformation.

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29. V. N. Krivobok and C. Wells, "Alloys of Iron, Manganese and Carbon—Part V," *TRANSACTIONS, American Society for Steel Treating*, Vol. 21, 1933, p. 807.
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31. C. R. Wohrman, "Heterogeneity of Iron-Manganese Alloys," *Transactions, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division*, Vol. 80, 1928, p. 197.
32. E. A. Owen and A. H. Sully, "The Equilibrium Diagram of Iron-Nickel Alloys," *Philosophical Magazine*, Vol. 27, Series 7, 1939, p. 614.
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DISCUSSION

Written Discussion: By David Harker, Research Laboratory, General Electric Co., Schenectady, N. Y.

In the course of their outstanding work on the equilibrium states of iron-manganese alloys, the authors obtained an extremely accurate set of lattice constants for the alpha and gamma phases. From these values it is possible to obtain excellent values for the effective radius of manganese in both twelve and eight coordination.

When the values of a_0 for the face-centered cubic gamma phase are plotted against atom per cent of manganese the points lie very close to a straight line, which extrapolates to a value of $a_0 = 3.681 \text{ \AA}$ for pure manganese. This value indicates a radius for the manganese atom of 1.30 \AA when in twelve coordination. When the line is extrapolated to pure iron, the lattice constant is found to be $a_0 = 3.566 \text{ \AA}$, in satisfactory agreement with other values in the literature for iron in twelve coordination. It seems reasonable, therefore, to accept 1.30 \AA as the proper value to use for manganese in twelve coordination. Using Goldschmidt's factor of 0.97 for converting the twelve coordination radius of a metal atom to that for eight coordination, the value 1.26 \AA is obtained for manganese. This radius can be compared with that indicated by the values of the alpha phase lattice constants.

A plot of the body-centered cubic alpha phase lattice constants against atom per cent manganese does not result in a straight line. The curve is concave upward to about 1 per cent manganese and then straightens out so that a straight line can be drawn through the points from 1 to 3 per cent. It frequently happens that the curve of lattice constant against atom per cent for a binary alloy drops below the straight line joining the points for the pure constituents, but parallels this line along an almost straight path, rising to meet it over a small range of compositions at either end of the composition

range. If it is assumed that this sort of thing is taking place in the case at hand, it is possible to infer a manganese radius for eight coordination from the data. Extrapolating the line from 1 to 3 atom per cent manganese to pure manganese a value $a_0 = 2.921 \text{ \AA}$ for the body-centered cubic structure is obtained and this leads to a radius of 1.27 \AA for eight coordination, in excellent agreement with that obtained above. (The correction resulting from raising the line so that it passes through the lattice constant for pure iron at zero per cent manganese changes this radius by only one part in ten thousand.)

These radii for manganese are in good accord with its alloying properties and probably should be given precedence over other values to be found in the literature.

Written Discussion: By Ralph Hultgren, assistant professor of physical metallurgy, University of California, Berkeley, Cal.

The authors are to be congratulated for this work which establishes phase boundaries for the alpha-gamma transformation in the iron-manganese system, which should stand for a long time. It is interesting that in Hansen's⁹ compilation several pages are devoted to discussing a large number of papers dealing with this transformation without arriving at a conclusion. The results given in this paper show why previous methods were not adequate to establish the phase boundaries.

The success of the present authors is to be attributed to their use of the X-ray method, their careful preparation of the alloys, their precise annealing conditions, and the length of time for their anneals.

Sharp lines in back reflection X-ray pictures are obtained only from phases which are precisely homogeneous and free from internal strain. This is good evidence that the phase concerned is in equilibrium. Furthermore, patterns of different phases are sharply distinguished from each other so there is no possibility of confusion. The microscope is unable to establish homogeneity of a phase, and different phases may be confused. Other methods, such as cooling curves, rely on deductive reasoning, which must often be complex. Several interpretations are sometimes possible.

The annealing of powders in small, sealed capsules for periods up to two years seems to be the best available method for attaining equilibrium and retaining it on quenching to room temperature. The small containers should be uniform in temperature so that distillation of the volatile manganese is avoided. The quench of a powder is the most rapid attainable.

The explanation of the supersaturated alpha and epsilon phases as unstable appears to be clear. The writer has had experience with supersaturated alpha phase in the iron-palladium system.¹⁰ There, too, the gamma formed supersaturated alpha at high iron contents and the diffraction lines were broad, indicating strain. At higher palladium contents the gamma could be retained. No epsilon was formed. In some cases, lines of supersaturated alpha occurred along with lines of equilibrium alpha; so the situation is exactly analogous.

⁹M. Hansen, "Aufbau der Zweistofflegierungen," Julius Springer, Berlin.

¹⁰R. Hultgren and C. A. Zapffe, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 133, 1939, p. 58-68.

There is little to criticize in a paper like this. On Fig. 5, it should be stated that the transformation is between gamma and supersaturated alpha that is measured, not gamma and alpha. I am inclined to think that in a practically useful region of a diagram results would better be plotted in weight per cent rather than atomic per cent, though, as they note, in this case there is little difference.

Written Discussion: By Alden B. Greninger, General Electric Company, Lamp Department, Cleveland.

Messrs. Troiano and McGuire have presented here a fine example of the determination of an equilibrium diagram whose evaluation is made complicated by the presence of martensite transformations. In a case of this type, a complete solution to the problem really demands not only the location of the equilibrium phase boundaries, but also the location of A_r'' temperatures and temperatures for the beginnings of the reverse transformation. This information the authors have provided and summarized in Figs. 2 and 5 and in their statement that high velocity thermal analysis showed A_r'' temperatures for all alloys containing more than 3.2 per cent manganese to be independent of cooling velocity. Additional data that one would like to have are curves showing temperatures for the "ending" of martensite transformation on cooling and of the reverse transformation on heating.

One is impressed with the thoroughness of the authors' analysis and cannot help but contrast it with the quite impossible equilibrium diagram recently proposed by Bradley and Goldschmidt¹¹ for the analogous iron-nickel system. The iron-nickel¹² and iron-manganese systems actually have the same type of equilibrium diagram. In both of these systems we have a martensite structure that is body-centered cubic, and Troiano and McGuire have conservatively followed Owen and Sully's nomenclature (from their work on the iron-nickel system) in labeling this structure "supersaturated alpha" to distinguish it from the alpha phase, which is also body-centered cubic. My own opinion is that future confusion and misunderstanding would be less likely if a separate symbol—for example, alpha prime—were used to designate this structure.

The pertinent generalizations made by the authors (third paragraph, page 355) should be thoroughly digested by all investigators dealing with phase transformations and equilibria in alloy systems. Far too seldom is adequate recognition given to the fact that martensite transformations occur in many alloy systems, that their most important behaviors have been well established, and that they constitute a mode of transformation entirely different from that involving equilibrium phases. Some of the generalizations that may be made regarding martensite transformations are:

1. The transformation is "diffusionless," involving no change in chemical composition. There is no nucleation and no growth; rather, small discrete volumes of the parent metastable solid solution suddenly change crystal structure by a process of homogeneous shear.¹³ Thus, each plate-like volume after trans-

¹¹A. J. Bradley and H. J. Goldschmidt, *Journal, Iron and Steel Institute*, Vol. 140, 1939, p. 11.

¹²E. A. Owen and A. H. Sully, *Philosophical Magazine*, Vol. 27, 1939, p. 614.

¹³A. B. Greninger and A. R. Troiano, *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 145, 1941, p. 289.

formation is a single crystal (one "grain") of martensite. All martensite microstructures have a similar appearance. The shape of the martensite "grain" is that of a plate, and of course on a polished surface the structure is acicular. In general, the lower the temperature at which the structure is formed, the more perfect is the acicular microstructure.

2. The transformation progresses (that is, more and more discrete volumes suddenly transform) only while the specimen is cooling; transformation ceases if the temperature drop is interrupted. Thus, time is not a factor; the transformation is dependent only on temperature change.

3. The transformation cannot be suppressed, nor can the temperature of its beginning be depressed, by increasing the cooling or quenching velocity to the very highest attainable.^{14, 15, 16}

4. The martensite structure is never an equilibrium condition, although certain of these structures may persist indefinitely at or near room temperature.

5. If a certain metastable solid solution will, on cooling, begin to form martensite near room temperature, then deformations of the solid solution at room temperature will produce martensite. (Two well known alloys in which this behavior is utilized extensively in industry are "18-8" stainless steel and Hadfield's manganese steel.) Also, certain martensite structures may themselves be transformed to a different crystal structure by deformation. Troiano and McGuire have shown this to be true for epsilon martensite in the iron-manganese system; beta prime martensite in the copper-aluminum system also shows this behavior.¹⁴

6. In certain alloy steels, the aging of the metastable solid solution (austenite) at some temperatures (for example, room temperature) above A_r'' will result in a substantial lowering of A_r'' on subsequent cooling. Gordon and Cohen¹⁷ have observed this behavior in 18-4-1 high-speed steel, and Troiano¹⁸ has observed it in high-carbon, high-chromium steel. This stabilizing effect of aging does not occur in plain carbon steels or nonferrous alloys.

7. All recorded martensite transformations have been shown to be reversible except that in iron-carbon alloys (see discussion of Ref. 14). Here the speed of martensite decomposition is too great to permit a demonstration of reversibility.

8. The martensite structure always has a greater hardness than that of the parent solid solution from which it formed. However, extreme hardnesses are associated with martensite only in steel containing appreciable amounts of carbon. An exception to this is the series of iron-cobalt-tungsten alloys developed by W. P. Sykes¹⁹ wherein hardnesses of 67 Rockwell C result from high-temperature aging of a martensite structure.

¹⁴A. B. Greninger, *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 133, 1939, p. 204.

¹⁵A. B. Greninger, "The Martensite Thermal Arrest in Iron-Carbon Alloys and Plain Carbon Steels," *TRANSACTIONS, American Society for Metals*, Vol. 30, 1942, p. 1.

¹⁶A. B. Greninger and A. R. Troiano, *TRANSACTIONS, American Society for Metals*, Vol. 28, 1940, p. 537.

¹⁷P. Gordon and M. Cohen, "The Transformation of Retained Austenite in High Speed Steel at Subatmospheric Temperatures," *TRANSACTIONS, American Society for Metals*, Vol. 30, 1942, p. 569.

¹⁸A. R. Troiano, discussion of Ref. 17.

¹⁹W. P. Sykes, "The A_r'' Range in Some Iron-Cobalt-Tungsten Alloys," *American Society for Metals 1942 Preprint No. 3*.

Oral Discussion

F. M. WALTERS, JR.:²⁰ The authors are to be congratulated on their very careful and thorough investigation. The confirmation of the findings of my associates and myself on this interesting system is very gratifying.

However, I wish the authors would give their reasons for believing that the light streaks in Fig. 4 are equilibrium alpha rather than regions in which the separation of phases is not so far advanced as it is in the background.

In regard to the 200-degree Cent. treatment of the alloys, it is surprising that the dense close-packed epsilon should transform to alpha. I would like to suggest the possibility that the cold-worked gamma transformed to alpha while the epsilon remained more or less intact. Since the gamma lines were not observed in the sample, the absence of epsilon lines may not be conclusive evidence of the absence of this phase.

Authors' Reply

The authors wish to thank the various discussers for their interest and valuable contributions to the paper.

We were gratified to be able to join Dr. Walters and his co-workers in confirming the general features of the original cooling curves of Rumelin and Fick, and also to be able to extend and interpret our high speed thermal analysis in terms of the martensite transformation, in addition to determining the true solubility limits of the alpha and gamma phases.

The reasons for believing that the light constituent in Fig. 4a is equilibrium alpha has been clearly stated in the paper. The authors recommend careful re-reading of pages 349 to 352. The fact that a close-packed structure should transform to one of less dense atomic packing (in this case epsilon \rightarrow alpha) is not too surprising. Indeed the literature is full of just such cases. One has only to refer to the universally well known austenite \rightarrow martensite transformation in steel, not to mention the gamma \rightarrow alpha transformation in pure iron. In fact the same situation is evident in the cold working of 18-8 stainless or Hadfield manganese steel as well as in many other alloys.

Dr. Harker's analysis of our lattice constant data is very interesting. The extrapolation of the equilibrium alpha lattice constants from 3 to 100 atomic per cent manganese may, at first, appear to be over-optimistic. On the other hand, the equilibrium gamma lattice constant versus atomic per cent manganese curve allow a much stronger extrapolation to be made. However, the fact that the value for the atomic radius of manganese with a co-ordination number 8 (body-centered cubic) obtained by extrapolating the alpha curve is practically the same as the value that results from applying Goldschmidt's correction factor of 3 per cent contraction to the extrapolated gamma value lends weight to what might normally be considered dangerous extrapolation. It is hoped that Dr. Harker will be able, in the near future, to present some applications of these new radii for manganese.

²⁰Division of Physical Metallurgy, Naval Research Laboratory, Anacostia Station, Washington, D. C.

Dr. Hultgren has presented an excellent brief summary of the power of X-ray diffraction in the study of phase relationships in the solid metallic state. The reference to the iron-palladium system is pertinent, especially with respect to the existence of supersaturated and equilibrium alpha in the same specimen. In labeling Fig. 5 the authors avoided the statement that the transformation is between gamma and supersaturated alpha because the alpha formed in the very low manganese content specimens is not supersaturated (compare Figs. 5 and 2). The term alpha as used in Fig. 5 was intended to be interpreted in its most general sense.

Dr. Greninger's rationalization of the criteria for the martensite type of transformation is a welcome contribution to the paper. Such an analysis has long been needed.

The authors were hesitant to employ a separate designation for supersaturated alpha, such as alpha prime. In fact, the use of such a term was studiously avoided. The reasons for this are subtle but nonetheless important. Regardless of the cooling velocity, alloys of less than approximately 3.2 per cent manganese are probably not supersaturated at room temperature. The precise solubility of manganese in iron at room temperature is, of course, not known, while those alloys of higher manganese content are definitely supersaturated. Now if the term alpha prime were substituted for supersaturated alpha then alpha prime would designate the martensite structure and by inference would imply that the alpha structure (obtained by even the most rapid cooling velocities) in the low manganese specimens is not the result of a martensite transformation. The authors do not feel that this is necessarily true. There is no reason to believe that supersaturation is a necessary condition of the result of a martensite transformation, and it is interesting to note that Dr. Greninger has not listed such a condition in his generalizations.

It is true that in the low manganese specimens the gamma \rightarrow alpha transformation temperature was not independent of the cooling velocity and hence one might conclude that it is not a martensite transformation. Such a conclusion based on only 3 cooling velocities (450, 3000, and 9000 degrees Cent. per second) would not be justified. If the critical cooling velocity were more than 3000 degrees Cent. per second no independence of cooling velocity would be observed. Additional experimental data are necessary before any further conclusions can be drawn.

THE INDUCTION FURNACE AS A HIGH TEMPERATURE CALORIMETER AND THE HEAT OF SOLUTION OF SILICON IN LIQUID IRON

BY JOHN CHIPMAN AND NICHOLAS J. GRANT

Abstract

A high frequency induction furnace containing 65 to 90 pounds of liquid metal is used as a calorimeter for determining the heat of solution of silicon in liquid iron. The temperature rise in the bath caused by the addition of a weighed amount of silicon is measured by a tungsten-molybdenum thermocouple. By comparing this rise with the temperature drop attending the addition of a weighed amount of iron, and with the aid of the known heat capacities of iron and silicon, a figure is obtained for the heat of solution of liquid silicon in liquid iron.

To distinguish between heat of solution and heat of deoxidation, samples taken before and after the addition were analyzed for silicon and oxygen. Taking the heat of deoxidation of iron by liquid silicon at 1600 degrees Cent. (2910 degrees Fahr.) as 148,200 calories evolved per mole of SiO_2 formed, the heat of solution of liquid silicon in liquid iron is found to be 29,000 calories evolved per gram atom of silicon.

From these results and supplemental data, the temperature changes accompanying the addition of several grades of ferrosilicon, with and without deoxidation, have been calculated as shown in Table V.

INTRODUCTION

OUR knowledge of the chemistry of reactions in liquid steel has been lacking in one important respect, namely, direct information on the heat effects of these reactions. Calculations based upon thermal measurements at lower temperatures can yield entirely dependable results in certain cases where complete data are available. In many cases, however, the data are not complete and the accuracy of the calculation suffers from the necessity of introducing assump-

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. Of the authors, John Chipman is professor of metallurgy, and N. J. Grant is instructor of metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. Manuscript received July 6, 1942.

tions or approximations. A method for the direct measurement of heat effects at high temperatures would make it possible to fill in these gaps in existing information.

One of the most productive methods for finding the heat of reaction at high temperature is that based upon the van't Hoff equation. This requires a knowledge of the equilibrium constant at several temperatures and when accurate equilibrium data are available over a range of temperatures the calculated heat of reaction is entirely dependable. It happens more frequently that the precision of high temperature equilibrium measurements is not adequate for an exact calculation of the heat effect, and an independently determined heat of reaction would be helpful not only in evaluating the equilibrium data but also in extending it to temperatures beyond those of direct observation.

Work of Körber and Oelsen—An ingenious method has been used by Körber and Oelsen (1)¹ to determine the heat of formation of molten iron-silicon and nickel-silicon alloys, including compositions corresponding to the intermetallic compounds. Since the experiments to be reported in this paper will be directly compared with their results, it will be pertinent to examine briefly the method they employed. Their method depends upon two series of experiments in each of which the heat content of the material at high temperatures is measured by quenching it into a water calorimeter operating at room temperature and measuring its temperature rise.

The first series of experiments determined only the heat of formation of the alloys at room temperature. Liquid iron at 1600 degrees Cent. (2910 degrees Fahr.) was poured on solid silicon (97 to 98 per cent) contained in a silica crucible at room temperature. The crucible containing the resulting molten mixture was transferred to a calorimeter to determine the total heat content relative to the calorimeter temperature, 20 degrees Cent. (70 degrees Fahr.). This heat quantity, minus the heat introduced in the added iron, which was determined separately, gave the heat of formation of the resultant iron-silicon alloy at 20 degrees Cent. (70 degrees Fahr.). Results obtained in this way in the range 0 to 22 per cent silicon are shown in the solid circles of Fig. 1.

At higher silicon contents the procedure was reversed and liquid silicon at 1600 degrees Cent. (2910 degrees Fahr.) was poured over

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

iron wire. In this case the heat introduced by the molten silicon is subtracted from the total heat measured to give the heat of formation of the alloy. Results in the range 40 to 100 per cent silicon are shown by the open circles of Fig. 1.

All of these results are adequately fitted by two straight lines which intersect at a composition corresponding to the compound FeSi and a heat evolution of 9.6 kilocalories. Since this corresponds to one-half gram-atom of each element, the heat of formation is double this quantity or 19,200 calories per mole at 20 degrees Cent. (70 degrees Fahr.).

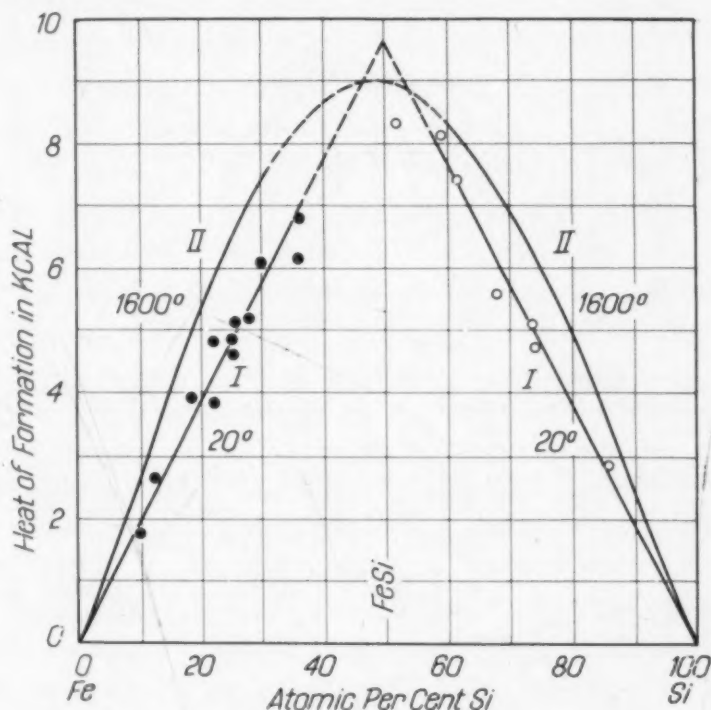


Fig. 1—Heat of Formation of Iron-Silicon Alloys (Körber and Oelsen). Curve I at 20 Degrees Cent. Curve II, 1600 Degrees Cent. Solid Circles—Molten Iron Added to Solid Silica. Open Circles—Molten Silica Added to Solid Iron.

In the second series the heat content of a series of molten iron-silicon alloys at 1600 degrees Cent. (2910 degrees Fahr.) was determined relative to the calorimeter temperature, 20 degrees Cent. (70 degrees Fahr.). The results are shown in Fig. 2 in which the composition in atomic per cent is plotted horizontally and the heat content per gram-atom of alloy is shown vertically. The straight line which connects the two extremities corresponding to pure iron and pure silicon represents the heat content that would have been

observed if the two elements had been quenched separately in proportions corresponding to the alloy. The difference between the straight line and the experimental curve represents the difference between the heat of formation of the alloy at 1600 degrees Cent. (2910 degrees Fahr.) and its heat of formation at 20 degrees Cent. (70 degrees Fahr.). Accordingly in Fig. 1, a second line can be drawn differing from the first in the same way that the straight line of Fig. 2 differs from the experimental curve. This second line (Curve II, Fig. 1)

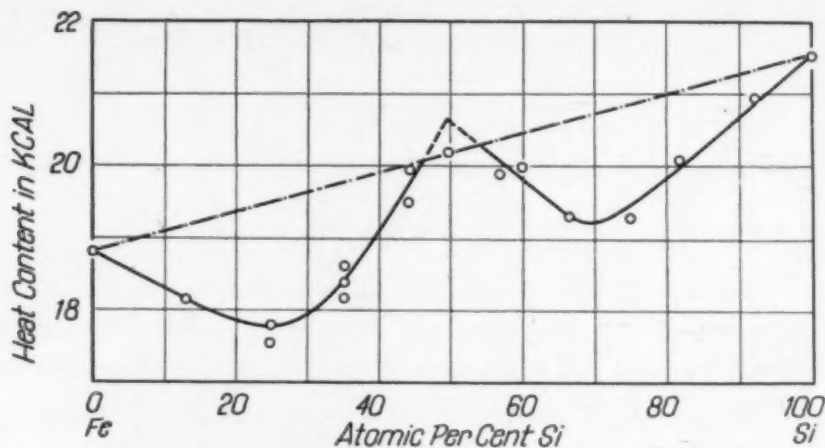


Fig. 2—Heat Content Per Gram Atom of Iron-Silicon Melts at 1600 Degrees Cent. Relative to 20 Degrees Cent. (Körber and Oelsen).

represents the heat of formation of the liquid alloy from the liquid metals at 1600 degrees Cent. (2910 degrees Fahr.).

The heat evolved when a limited amount of liquid silicon is added to a large amount of liquid iron, the differential heat of solution, is determined by the slope of the left-hand branch of Curve II in Fig. 1. This amounts to 28,500 calories per gram-atom of silicon and is essentially constant in the range 0 to 11 per cent silicon. This is the quantity which is to be compared with the results of our direct experiments described later in this paper.

EXPERIMENTAL METHOD

The use of a high frequency induction furnace as a calorimeter for obtaining direct data at high temperatures might reasonably be expected to offer considerable difficulty, especially in view of the elaborate precautions which must be employed in accurate calorimetry (2) at room temperature. Such difficulties were in fact encountered and it will be well at the outset to state the tentative conclusion, based upon a limited amount of experimentation, that the method here

employed is not applicable to all of the reactions in liquid steel which we should like to study. For reactions which occur homogeneously within the molten metal, the method yields reproducible results whose accuracy may be described as something better than a rough approximation.

For this purpose the induction furnace has certain peculiar advantages: the heat losses by radiation and conduction can be closely balanced by control of power input; the method of heating provides a rapid stirring action in the bath; the molten iron serves simultaneously as the calorimetric fluid, the heating element, and the solvent in which the reaction occurs. The lining of the furnace must obviously be made of materials which are as inert as possible toward the reactants involved.

A high frequency induction furnace with a capacity of 150 pounds was used. This furnace was charged with only 65 to 100 pounds of metal so that the bath surface was down in the crucible where it could not chill as readily. A definite sized opening was allowed in the top, large enough for additions, sampling and temperature measurement. This opening remained fixed for the entire run, allowing fairly constant radiation and convection losses.

The crucible was made of high grade crushed silica ganister which was tamped in about a steel tube. The tube was then withdrawn and the lining was fused to give a very solid, homogeneous crucible. These crucibles lasted a long time under the acid conditions used, even at very high temperatures.

TEMPERATURE MEASUREMENTS

Temperatures were measured by means of tungsten-molybdenum thermocouples inserted into the molten bath in fused silica protection tubes. The couples were made by twisting the molybdenum wire around the tungsten (both were 0.020 inch in diameter) and arcing the tip to a carbon electrode. The couples were then annealed in hydrogen at a temperature just below the melting point of the molybdenum (2500 degrees Cent.) (4530 degrees Fahr.). They were then calibrated against a previously calibrated platinum, platinum-rhodium couple in the range from 1400 to 1650 degrees Cent. (2550 to 3000 degrees Fahr.).

The thermocouple holder was a water-cooled tube which was constructed in such a fashion that the cool water from the tap kept

the cold junction at the temperature of the water. Once the holder was placed in the furnace for a reading it was not removed until a complete determination had been made. This was done so that the cooling effect of the couple holder would not be a variable with its insertion into the furnace for each temperature determination. Thermocouples of this type have been used in this laboratory during the past five years and have been found highly satisfactory for measuring induction furnace temperatures. The silica protection tubes are corroded by undeoxidized iron but not rapidly enough to prevent their use. In deoxidized metal their life is quite satisfactory.

The e.m.f. of the couple was measured to ± 0.002 millivolt which corresponds to a precision of about 0.3 degree Cent. Though the absolute accuracy of the couple is not better than ± 5 degrees Cent., the relative accuracy, which is the important thing in calorimetry, is sufficient to measure temperature changes with an uncertainty of something less than 1 degree.

SAMPLING

The metal samples used for analyses were obtained by dipping a small long-handled mold. The molds were made of 2-inch lengths of half-inch pipe, split longitudinally to simplify removal of the sample, and were held together with iron wire. To provide for rapid cooling of the samples, heavy-walled pipe was used. All molds were painted with a magnesia slurry to aid in removal of the samples.

ANALYSIS

All oxygen analyses were made by the vacuum fusion method. In most cases duplicate samples agreed within 0.001 per cent oxygen, with additional checks being made where the disagreement was appreciably greater.

All samples were analyzed for silicon by perchloric acid dehydration.

TYPICAL EXPERIMENT

Heat D-49 will be described to indicate the procedure used in all experiments. One hundred pounds of ingot iron were melted and slowly brought to as constant temperature as possible, temperature readings being taken at intervals to note the progress. When two consecutive readings indicated the temperature to be holding constant, a metal sample was dipped. Several minutes were allowed to pass

and a temperature was again obtained. About 30 seconds later 227 grams of silicon (98 per cent silicon metal was used) in a thin sheet-iron container were added and dissolved into the bath. The stirring action in the furnace thoroughly mixed the bath in a matter of a fraction of a minute. Forty-five seconds after the addition, the change in temperature of the bath was measured and then a second metal sample was obtained. After waiting for a period of time the same procedure was repeated, using in some cases 454 grams and in other cases 113.5 grams of silicon ($\frac{1}{4}$, $\frac{1}{2}$ and 1-pound additions) to get the heat effects. The first addition caused a considerably greater temperature rise than did any of the later ones. This was ascribed to heat of deoxidation which is much larger than the heat of solution. It was for the purpose of distinguishing between these two effects that samples were taken before and after each addition.

To get the heat capacity of the furnace, ingot iron rods of known weight were melted into the bath before any silicon had been added and the temperature change noted. From this observation and the known weights and thermodynamic values of the iron, a calculation was made to determine the calorimeter heat capacity.

SUPPLEMENTAL DATA

The calculation of the results requires a knowledge of the heat capacities, heats of transition and of fusion of both iron and silicon between room temperature and the temperatures of the experiments. A large amount of experimental data is available for iron and a more limited amount for silicon. It seems unnecessary to review all of these data here in view of the recent competent reviews by Austin (3) and Kelley (4). The experiments of Körber and Oelsen (1) also included determinations of the heat contents of iron and silicon

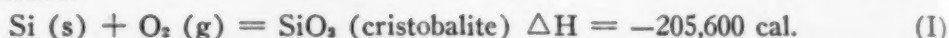
Table I
Thermal Data on Iron and Silicon

Source	Heat Content Difference $H_{1600} - H_{27}$ Calories per Gram		Heat of Fusion of Si Calories per Gram	Specific Heat of Liquid cal/deg/gram	
	Iron	Silicon		Fe	Si
Körber and Oelsen	335	767	396	0.40
Austin	337	0.185
Kelley	326	746*	342	0.146
Selected	335	767	396	0.161	0.40
(per gram)					
Selected	18700	21500	11100	9.0	11.2
(per gram-atom)					

* Extrapolated value using heat of fusion of silicon of 396 cal/gram.

at 1600 degrees Cent. (2910 degrees Fahr.). All of these data are summarized in Table I which shows also the selected values used in our calculations. It should be pointed out that the greatest uncertainties are attached to the heat capacities of the liquid metals which may be in error by 10 per cent or more. This does not introduce a 10 per cent uncertainty into the result for the reason that the heat capacity of the calorimeter was determined directly by addition of solid iron whose total heat absorption is known within about 2 per cent.

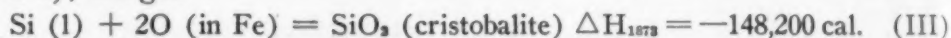
The heat of formation of silica was recently redetermined by Roth and Becker (5) who report the following value at room temperature.



By means of the heat capacity data of Kelley's tables (4) and the data of Table I, this becomes, at high temperature



Finally, using Marshall's (6) data for the change: $\text{O}_2 \text{ (g)} \rightarrow 2\text{O (in Fe)}$, we get



This is the value which must be subtracted from the total heat effect on tests where both deoxidation and solution resulted in order to get only a solution heat effect.

EXPERIMENTAL RESULTS

Two determinations of the heat capacity of the furnace calorimeter were carried out by adding weighed amounts of iron rod and measuring the accompanying temperature drop. As shown in Table II, both experiments gave the same result, 2.5 kilocalories per degree for the effective heat capacity of the furnace.

A summary of all experiments involving addition of silicon is given in Table III and a graphical record of each experiment is shown in Fig. 3. Since it was found impractical to maintain furnace temperatures exactly constant either before or after an addition, the observed drifts were extrapolated to the time of the addition and the offset at this time was taken as the temperature rise. It was occasionally observed that a downward trend occurred after the silicon addition even when a very careful adjustment had been made and the power input was constant. This was ascribed to a change in emissivity of the liquid metal surface; the thin scum formed after

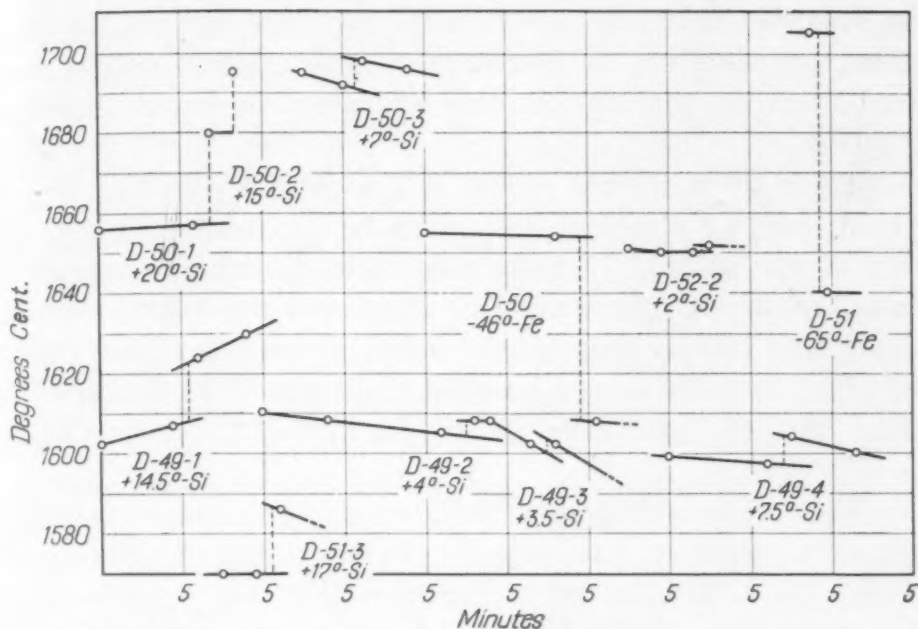


Fig. 3—Temperature Changes on the Addition of Solid Iron or Silicon to Liquid Iron.

Table II
Determination of the Heat Capacity of the Furnace

Heat	Wt. of Bath Grams	Initial Temp. of Bath, °C.	Iron Added, Grams	ΔT °C.	Heat Capacity— Kilocalories per Degree		
					Total	Liquid Fe	Furnace
D-50	30,870	1654	1020	—46	7.47	4.97	2.50
D-51	28,600	1705	1350	—65	7.10	4.61	2.49

Table III
Summary of Experimental Heats

Heat	Test	Sample	Bath Wt. Grams	Temp. °C.	Additions Grams		$+ \Delta T$ °C.	Per Cent Oxygen	Per Cent Silicon	Heat of*
					Si	Fe				
D-49	1	2	43,720	1610	227	59	0.123	0.004	D.S.
		3					14.5	0.021	0.34	
D-49	2	4	43,770	1604	232	59	0.030	0.02	S.
		5					4.0	0.026	0.55	
D-49	3	5	43,850	1599	227	76	0.026	0.55	D.S.
		6					3.5	0.018	1.03	
D-49	4	8	43,950	1597	458	132	0.006	0.88	S.
		9					7.5	0.007	1.90	
D-50	1	1	30,800	1657	114	50	0.141	0.002	D.S.
		5					20.0	0.043	0.28	
D-50	2	5	30,920	1680	227	66	0.043	0.28	D.S.
		6					15.0	0.034	0.96	
D-50	3	6	31,060	1691	227	64	0.034	0.96	D.S.
		7					7.0	0.017	1.68	
D-51	1	11	30,600	1640	114	55	0.133	0.014	D.S.
		12					18.0	0.029	0.34	
D-51	2	13	30,650	1650	114	53	0.021	0.14	S.
		14					2.0	0.022	0.51	
D-51	3	15	30,600	1570	455	78	0.007	0.48	S.
		16					17.0	0.005	1.97	

*D = Heat of Deoxidation.

S = Heat of Solution.

D.S. = Heat of Deoxidation and Solution.

silicon deoxidation has a higher emissivity than that of the clean metal surface resulting in greater heat losses. Best results were obtained when the surface condition was the same before and after the addition.

Study of the analytical results in Table III shows that in only four cases can the observed heat effect be ascribed entirely to the solution of the silicon. In these four tests the oxygen content of the metal remained substantially constant and the silicon recovery was practically 100 per cent of that added. In all other cases the observed effect includes some heat of deoxidation. The data and calculations on these four tests are shown in the first four lines of Table IV.

In three other cases both deoxidation and solution occurred. In these cases a correction was made for the heat effect due to deoxidation using the value obtained in Equation III. These values are in the last three lines of the table. Two other tests were made, but due to the excessive porosity of the samples it was impossible to get any good checks on the oxygen values; therefore these tests were left out of the calculations.

Table IV
Data and Calculations on Heat of Solution of Silicon in Iron

Test	Wt. of Bath Grams	Temp. Degrees Cent.	Additions Grams		Si Recovered Grams	Per Cent Oxygen Removed
			Si	Fe		
D-49-2	43,770	1604	232	59	232	0.004
D-49-4	43,950	1597	458	132	458	0.000
D-51-2	30,650	1650	114	53	113	0.000
D-51-3	30,600	1570	455	78	455	0.002
D-49-3	43,850	1599	227	76	209	0.008
D-50-1	30,800	1657	113	50	86	0.098
D-50-3	31,060	1691	227	64	226	0.017

Test	$+\Delta T$ Cent. Degrees	Total	Deoxidation Heat Evolved,	Solution Kilocal.	Cal/gram-atom $-\Delta H$
D-49-2	4.0	236.8	4.8	232.0	28,100
D-49-4	7.5	468.5	468.5	28,770
D-51-2	2.0	121.0	121.0	30,000
D-51-3	17.0	497.8	497.8	30,800
D-49-3	3.5	234.0	16.1	217.9	29,200
D-50-1	20.0	257.5	140.1	117.4	38,300
D-50-3	7.0	258.3	24.5	233.3	29,000
Average (omitting D-50-1)					29,300

SAMPLE CALCULATIONS

Test 3, Heat D-50, is used here as a sample calculation in determining the heat of solution of silicon in liquid iron. This test involved a combined heat of deoxidation and heat of solution. Refer to Table III for the figures used.

Silicon added = 8.09 mols.

Silicon recovered = 8.02 mols.

Iron added = 1.14 mols.

Oxygen removed = 0.165 mols.

Heat content of silicon per gram-atom (27-1698 degrees Cent.) = 22,596 cal.

Heat content of iron per gram-atom (27-1698 degrees Cent.) = 19,580 cal.

Heat capacity of calorimeter = 2500 cal/degrees Cent.

Heat capacity of liquid iron = 9.0 cal/g. atom degrees Cent.

$\Delta T = + 7$ degrees Cent.

Total Heat Effect:

	<i>Calories</i>
1. To raise iron addition to 1698 degrees Cent. = 1.14×19580	= 22,300
2. To raise silicon addition to 1698 degrees Cent. = 8.09×22596	= 183,000
3. To raise iron bath through 7 degrees Cent. = $55.7 \times 9.0 \times 7$	= 35,000
4. To raise calorimeter through 7 degrees Cent = 2500×7	= 17,500
5. Total heat	257,800
6. Heat of deoxidation $0.165 \times 148,200$	= 24,500
7. Heat of solution	= 233,300
8. Heat of solution per mol of silicon =	29,000

In the event that no deoxidation is indicated, the total heat effect (item 5) would be the value used in calculating the heat of solution.

DISCUSSION OF RESULTS

From the results of this work the value for the heat of solution of 1 gram-atom of silicon in liquid iron is:

$$\text{Si (1)} = \text{Si (in liquid Fe)}; \Delta H = - 29,300 \text{ cal.}$$

This value agrees very well with that of $-28,500$ calories found by Körber and Oelsen. It is difficult to estimate the absolute accuracy attained in these measurements. The uncertainty in the amount of heat absorbed in bringing iron from room temperature to furnace temperature is about 2 or 3 per cent; in the case of silicon it is somewhat larger. The effects of errors in determining ΔT are surprisingly small; thus an error of 1 degree gives a 6 per cent error in ΔH in test D-51-2 but only 1.5 per cent error in D-51-3, and intermediate errors in the other tests. We would therefore not be justified in expecting an accuracy better than about ± 5 per cent in the final result.

The heat evolution when silicon dissolves in iron or combines with oxygen has a marked technical importance in steelmaking. The temperature changes accompanying additions of various grades of silicon were calculated from the results of our data and the curves shown in Figs. 1 and 2. They are given in Table V and are plotted

Table V
Temperature Change From Additions of Silicon Metal and Ferrosilicon
to Molten Iron at 1600 Degrees Cent.
 (Heat Capacity of Furnace Assumed Negligible)

Silicon Added—%	Oxygen Removed =	0%	0.02%	0.05%	0.10%
		(Temperature Rise, Degrees Cent.)			
	98% Silicon Metal				
0.10		1.6	6.2	13.2	24.8
0.25		4.0	8.6	15.6	27.2
1.00		16.0	20.6	27.6	39.2
5.00		80.0	84.6	91.6	103.2
	75% Ferrosilicon				
0.10		0.3	4.9	11.9	23.5
0.25		0.8	5.4	12.4	24.0
1.00		3.0	7.6	14.6	26.2
5.00		15.0	19.6	26.6	38.2
	50% Ferrosilicon				
0.10	—	2.6	+ 2.0	+ 9.0	+ 20.6
0.25	—	6.4	+ 1.6	+ 5.2	+ 16.8
1.00	—	25.6	— 21.0	— 14.0	— 2.4
5.00	—	128.0	— 123.4	— 116.4	— 104.8

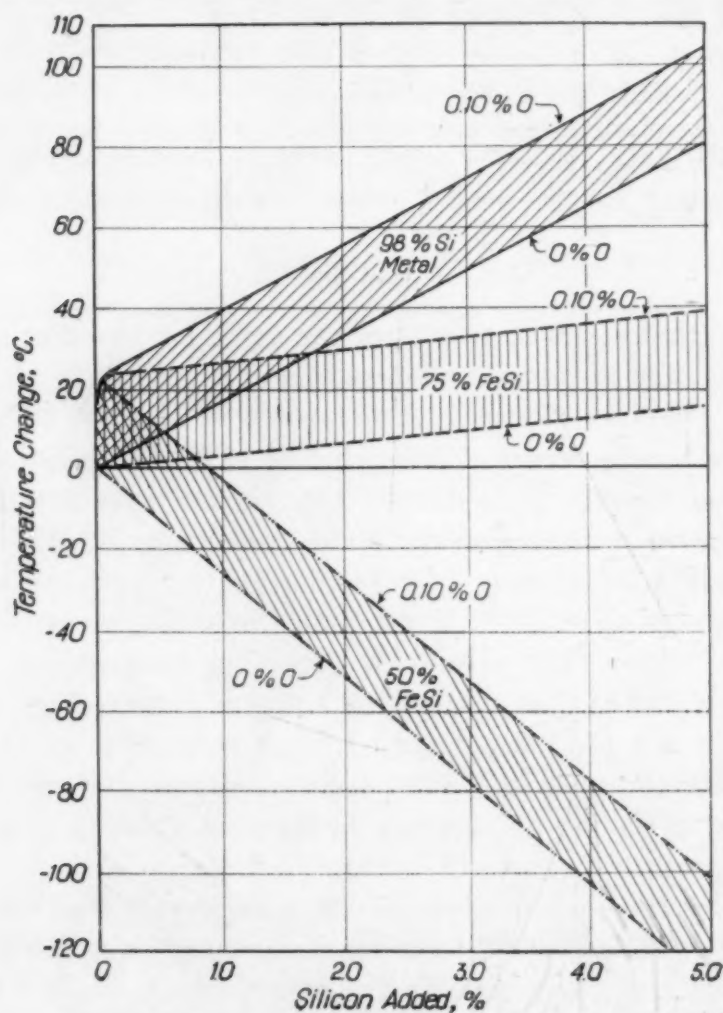


Fig. 4—Temperature Change by Addition of Silicon Metal or Ferrosilicon to Molten at 1600 Degrees Cent. (Heat Capacity of Furnace Assumed Negligible).

in Fig. 4. Temperature changes accompanying the deoxidation of iron with more than 0 per cent oxygen and less than 0.10 per cent are to be found between the limits of each shaded band in Fig. 4. It is interesting to note that even a small amount of deoxidation evolves enough additional heat to bring about quite a considerable change in temperature.

It must be pointed out that the use of Table V or Fig. 4 to estimate temperature changes due to additions of ferrosilicon to the ladle will meet with much difficulty since a subtraction of temperature must be made to correct for the heat absorbed by the ladle. Depending on the number of heats the ladle has poured and the amount of preheat, this value may vary over an extremely wide range. Table V is much more applicable to additions made in a heat-soaked furnace.

Thus the table shows that an addition of 1.0 per cent silicon as 98 per cent silicon metal results in a temperature rise of 16 degrees Cent. (60 degrees Fahr.) when no deoxidation takes place. With 75 per cent ferrosilicon this temperature increase is 3.0 degrees Cent., while with 50 per cent ferrosilicon there is a temperature drop of 25 to 26 degrees Cent. For the same addition of the various grades, but with 0.05 per cent oxygen removed by deoxidation, 98 per cent silicon gives an increase of 27.7 degrees Cent., 75 per cent ferrosilicon gives an increase of 14.6 degrees Cent. and 50 per cent ferrosilicon keeps the temperature drop to 14 degrees Cent.

This quite large heat evolution can be and is made use of in the manufacture of both 2.0 per cent silicon spring steels (S.A.E. 9155) and electrical sheet steels (up to 5.0 per cent silicon). The heat that is generated by using 75 per cent ferrosilicon allows temperature for reladling, which results in much better mixing of the silicon and iron without undue danger of running into exceedingly large ladle skulls which would cause not only loss of metal but also difficult pouring conditions.

Again, the large heat of solution of silicon in iron is utilized in the production of acid-resisting castings where mixtures of iron and high grade ferrosilicon are heated together. The reaction begins in the solid state, causing much more rapid fusion at a much lower temperature, but still resulting in a very hot melt.

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DISCUSSION

Written Discussion: By H. Edward Flanders, assistant research director, American Steel Foundries, E. Chicago, Ind.

Dr. Chipman and Mr. Grant have contributed again to our knowledge of thermochemistry and to the methods available in this paper when they give us an appreciation of the heat of solution of silicon in iron and show the adaptation of the induction furnace to calorimetry. By means of this method there should be a number of other determinations made which will be of value in practical metallurgy.

After careful perusal of their paper and particularly the data which it contains, I wish to make a few remarks which are based on some experience related to the subject of deoxidation.

In Fig. 3 of the paper under discussion there is given a schematic log of each test. From this and the discussion and the data in Table III, one may take some time composition data which, except for the upsetting effect of the further addition of silicon, may give some idea of the rate of removal of silicon dioxide from the liquid iron as it remains in the induction furnace. (Table A.)

Table A
Time Oxygen Content Data

Heat	Test	Sample	Time	Per Cent Oxygen
D-49	3	5	0	0.026
		6	1	0.018
		8	14	0.006
D-49	4	9	15	0.007
		5	0	0.043
D-50	2	5	0	0.043
D-50	3	6	1	0.034
D-50	3	7	9	0.017 (Time not clear).

The data are in qualitative agreement with an experiment in which the oxygen content of a silicon-killed iron dropped to a constant value of about 0.007 to 0.008 per cent. It was thought that the precipitated silica was merely being removed from the liquid iron during the approximately twenty minutes required.

In the data there are four cases where the oxygen content is between 0.005 and 0.007 per cent. One might consider this a solubility value for silicon dioxide under the conditions of test with the oxygen existing either as FeO or SiO₂ in the liquid metal.

In one of the instances there is recorded an oxygen content of 0.007 per

cent when 0.48 per cent of silicon is present. It is not likely that there is in any other case a concentration of oxygen greater than is present with the 0.007 per cent recorded which is capable of reaction with silicon when an equal or greater percentage of silicon is present. This means that in all cases where the silicon content was 0.48 per cent or more at this time of the silicon addition there is but little, if any, heat of deoxidation and that the heat effect may be attributed to the heat of solution. On this basis there are four tests which may be considered as direct determinations of the heat of solution of silicon in iron and these are listed in Table B.

Table B
Selection of Tests for Heat of Solution Determination

Heat No.	Test	Temperature Degrees Cent.	Range Per Cent Si	$-\Delta H =$ Heat of Solution Calories/Mol.
D-49	3	1601	0.55—1.03	27970
D-49	4	1601	0.88—1.90	28740
D-50	3	1694	0.96—1.68	31950
D-51	3	1578	0.48—1.97	30810
				Average 29870

The calculations were made using the data selected by Messrs. Chipman and Grant and check their values in the cases where this was determinable.

I have enjoyed studying this paper and wish to again compliment the authors on its content.

Authors' Reply

We wish to thank Dr. Flanders for his kind remarks. His choice of four out of our ten tests for making his calculations coincides at least in three cases with our own choice. Those samples which showed the same oxygen content before and after the silicon addition and which showed substantially 100 per cent recovery of the silicon added, were selected as being the tests in which no deoxidation or an insignificant amount of deoxidation had occurred.

In certain cases it was possible where only a very small amount of deoxidation had occurred to make a correction for this by means of known heat of reaction of silicon with oxygen. In any case the data will add up to about the same thing, that is approximately 29,000 calories, plus or minus about 5 per cent.

We should call attention to the fact that the oxygen remaining in the metal after the silicon addition which Dr. Flanders mentioned depends not only on the silicon content but on the temperature.

We should remark also that these studies were made simply to measure heat of reaction and no one should use the data in making any sort of equilibrium calculations. The surface of the bath was exposed to air and there was a certain amount of oxidation of the metal surface. This causes a slight error of course, but is balanced by adjusting the temperature carefully by controlling the power input to the furnace. There was silica floating on the surface in some cases. Our best results were obtained with a clean surface, free from silica scum. In cases where a substantial oxygen drop occurred, there was always silica formed on the surface of the bath. In other cases silicon was added with substantially no formation of silica on the surface.

THE TEMPERING OF TWO HIGH-CARBON HIGH-CHROMIUM STEELS

BY OTTO ZMESKAL AND MORRIS COHEN

Abstract

The kinetics and mechanism of the structural changes which accompany the tempering of 1 per cent carbon — 5 per cent chromium and 1.5 per cent carbon — 12 per cent chromium tool steels were investigated by means of magnetic, dilatometric and X-ray measurements. Austenitizing temperatures from 1700 to 2200 degrees Fahr. (925 to 1205 degrees Cent.), quenching in oil, air and lime, tempering temperatures from 70 to 1200 degrees Fahr. (20 to 650 degrees Cent.), and tempering times from several seconds to several hundred hours were studied.

In general, the hardened steels contain tetragonal martensite, retained austenite, and undissolved alloy carbides. During the early stages of tempering, the martensite decomposes from tetragonal to cubic, followed by precipitation of nonferromagnetic carbides. There is also evidence of stress relief in this range.

Time-temperature relationships for decomposing progressive percentages of the retained austenite by tempering are shown in the form of tempering transformation curves which are similar to the well known S-curves for the primary austenite transformation in alloy steels. The rate of retained austenite decomposition does not increase continuously with the tempering temperature. There is a range of relatively high isothermal reactivity between 500 and 600 degrees Fahr. (260 and 315 degrees Cent.), and the resulting product is believed to be bainite. Between 700 and 800 degrees Fahr. (370 and 425 degrees Cent.), the retained austenite is quite sluggish; but above 900 degrees Fahr. (480 degrees Cent.), the austenite becomes conditioned for transformation during the subsequent cooling. Depending upon the stability of the retained austenite and the amount available, the cooling trans-

This paper is based on a thesis submitted by Otto Zmeskal in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology, October, 1941.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. Of the authors, Otto Zmeskal is assistant professor of metallurgy, Illinois Institute of Technology, Chicago, and Morris Cohen is associate professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. Manuscript received July 20, 1942.

formation produces bainite or tetragonal martensite or both. With tempering temperatures above 1000 degrees Fahr. (540 degrees Cent.), isothermal decomposition sets in again and leaves correspondingly less austenite for transformation during the cooling. With certain combinations of hardening and tempering, the retained austenite decomposes during the heating to, the holding at, and the cooling from the tempering temperature.

Basically, the mechanism of the tempering process in these chromium tool steels is consistent with that reported for high speed steel, but is more varied in its details due to the wide range of retained austenite contents and stabilities obtainable in the chromium steels.

RECENT investigations (1-3)* on the tempering fundamentals of high speed steel have raised the question as to whether the same tempering phenomena occur in other high-alloy tool steels. Accordingly, two commercial high-carbon, high-chromium steels were selected for further tempering studies. These steels are used industrially for dies, punches and gages, and their tempering characteristics have received careful attention from a practical point of view. Several papers (4-8) have appeared on the heat treating, mechanical, and dimensional properties of these materials. However, there is a lack of detailed information on the kinetics and mechanism of the structural changes which attend the tempering of these steels.

The results of the present investigation may be divided into two interrelated parts: first, the study of the retained austenite transformation as a function of tempering time and temperature; and second, the study of the structural changes which take place during the heating to and cooling from the tempering temperature.

EXPERIMENTAL DETAILS

Steels Investigated—The steels used in this work were obtained through the courtesy of Mr. Norman I. Stotz of the Universal-Cyclops Steel Corporation. They were received as-annealed in two sizes— $\frac{5}{8}$ -inch square stock and $\frac{1}{4}$ -inch round stock. The compositions are shown in Table I. Before heat treatment, all of the bars

*The figures appearing in parentheses refer to the bibliography appended to this paper.

Table I
Chemical Analysis

Designation						C	Mn	Si	Cr	V	Mo	S	P	
1.5	Per	Cent	Carbon—12	Per	Cent	Chromium	1.60	0.33	0.32	11.95	0.25	0.79	0.010	0.018
1	Per	Cent	Carbon—5	Per	Cent	Chromium	1.00	0.61	0.17	5.31	0.27	1.13	0.013	0.014

were milled or centerless ground below any possible decarburization or surface imperfection.

Hardening Treatments—Hardening of the steels was carried out in a globar furnace at temperatures of 1700 to 2200 degrees Fahr. (925 to 1205 degrees Cent.) held to ± 3 degrees Fahr. Protection from decarburization during hardening was achieved with the aid of a carbonaceous muffle. Since the two steels are both oil and air hardening, these two quenching media were used, as well as lime cooling to simulate the air quenching of large sections.

Types of Measurement—The principal apparatus employed in this work was a combined magnet and dilatometer which permitted the simultaneous measurement of changes in magnetization and in length of a rod-shaped specimen $4\frac{1}{4}$ inches long by $\frac{1}{4}$ inch diameter. The apparatus has been described in detail elsewhere (10). Applied field strengths of 265, 770 and 1000 gauss were used. A relative accuracy of ± 0.1 per cent was obtained in the magnetic readings, while the changes in length were measured to ± 0.001 per cent. In the present paper, ballistic galvanometer deflections are plotted instead of a more absolute magnetic property since the investigation was primarily concerned with comparative changes. However, sufficient auxiliary data were obtained to convert all of the galvanometer deflections into absolute units of intensity of magnetization, if this should ever become desirable.

X-ray measurements were made on $\frac{7}{16}$ -inch cubes. A No. 2 Phragmen camera was used with chromium radiation from a modified Hägg X-ray tube (11). The specimens were ground to the curvature of the camera prior to the hardening in order that sharp lines would be produced in the photograms. After hardening, the surfaces of the specimens were etched for 15 to 20 minutes, electrolytically, in an aqueous solution of 5 per cent mixed hydrochloric and sulphuric acids. Some of the X-ray specimens were hardened and quenched in vacuo.

Procedure for Isothermal Tempering Experiments—In these runs, changes in magnetization were observed after tempering hard-

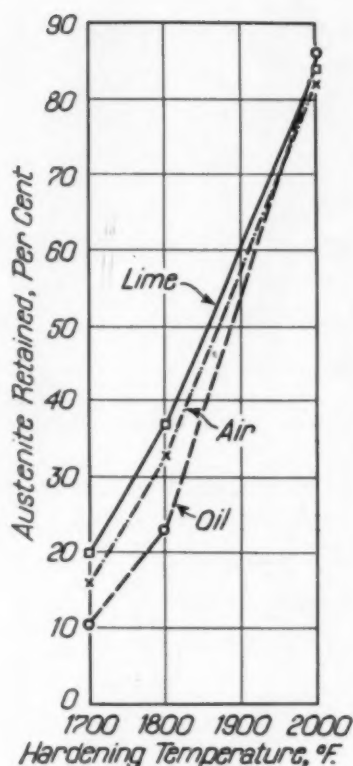


Fig. 1—Relation Between the Amount of Retained Austenite and the Hardening Temperature for a 1 Per Cent Carbon—5 Per Cent Chromium Steel Cooled as Shown.

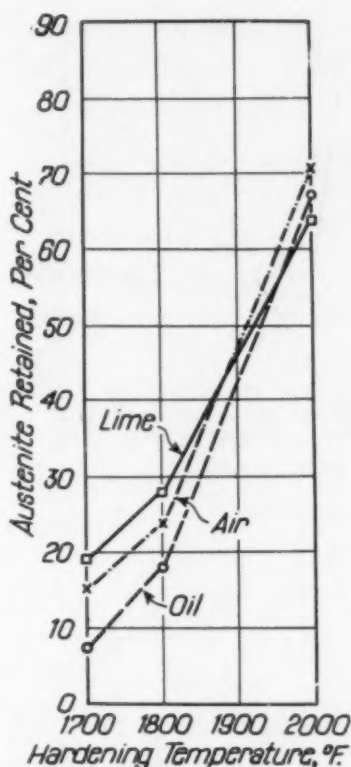


Fig. 2—Relation Between the Amount of Retained Austenite and the Hardening Temperature for a 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Cooled as Shown.

ened rod specimens at 400 to 1200 ± 3 degrees Fahr. (205 to 650 degrees Cent.) for times ranging from 7 seconds to several hundred hours. All such measurements were made at room temperature before and after repeated tempering. The effect of tempering time was found to be substantially independent of the number of individual tempering cycles composing the cumulative treatment provided that the rates of heating to and cooling from the tempering temperature were rapid. Consequently, liquid baths were employed for these tempering operations.

Procedure for Heating and Cooling Experiments—The structural changes during heating to and cooling from the tempering temperature were studied mainly by simultaneous magnetization and dilation measurements at intervals of 25 degrees Fahr. (14 degrees Cent.) during such heating and cooling. Various tempering temperatures, times, and cycles were used, but a constant heating and cooling rate of 5 degrees per minute was generally maintained.

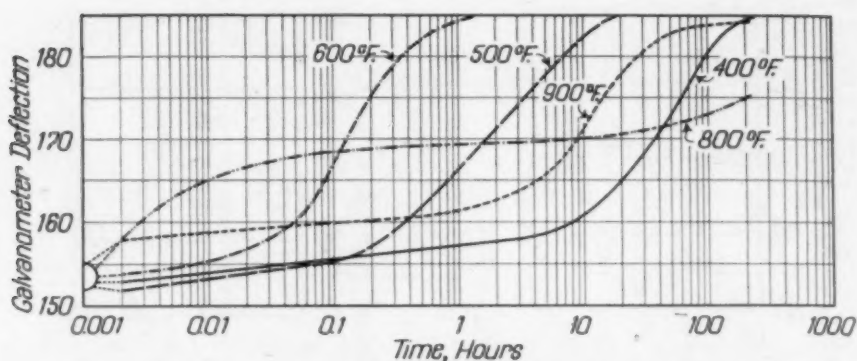


Fig. 3A—Tempering Curves for 1 Per Cent Carbon—5 Per Cent Chromium Steel Air-Cooled from 1700 Degrees Fahr. Measurements at Room Temperature in Field of 770 Gauss.

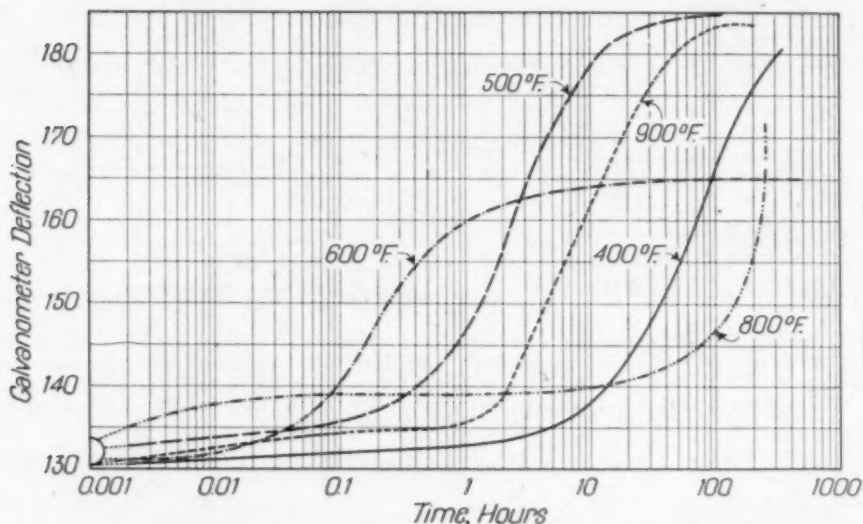


Fig. 3B—Tempering Curves for 1 Per Cent Carbon—5 Per Cent Chromium Steel Air-Cooled from 1800 Degrees Fahr. Measurements at Room Temperature in Field of 770 Gauss.

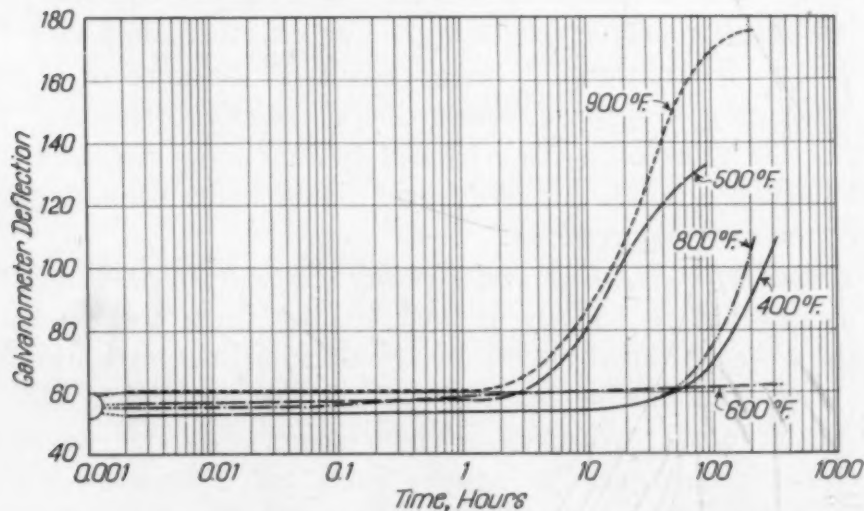


Fig. 3C—Tempering Curves for 1 Per Cent Carbon—5 Per Cent Chromium Steel Air-Cooled from 2000 Degrees Fahr. Measurements at Room Temperature in Field of 770 Gauss.

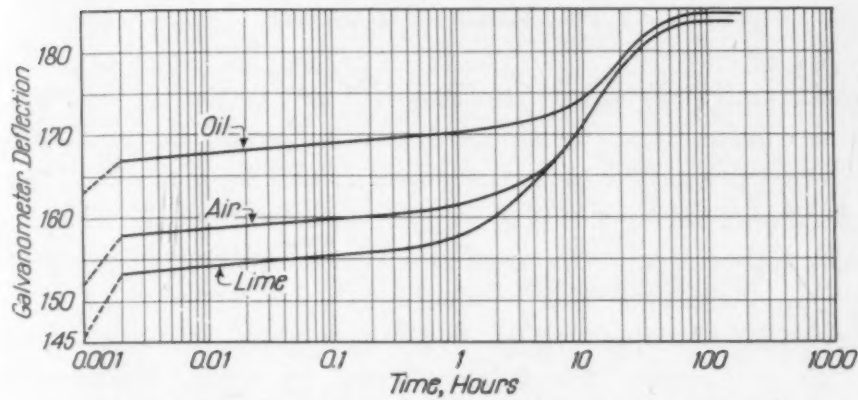


Fig. 4A—Tempering Curves at 900 Degrees Fahr. for 1 Per Cent Carbon—5 Per Cent Chromium Steel Cooled from 1700 Degrees Fahr. Measurements at Room Temperature in Field of 770 Gauss.

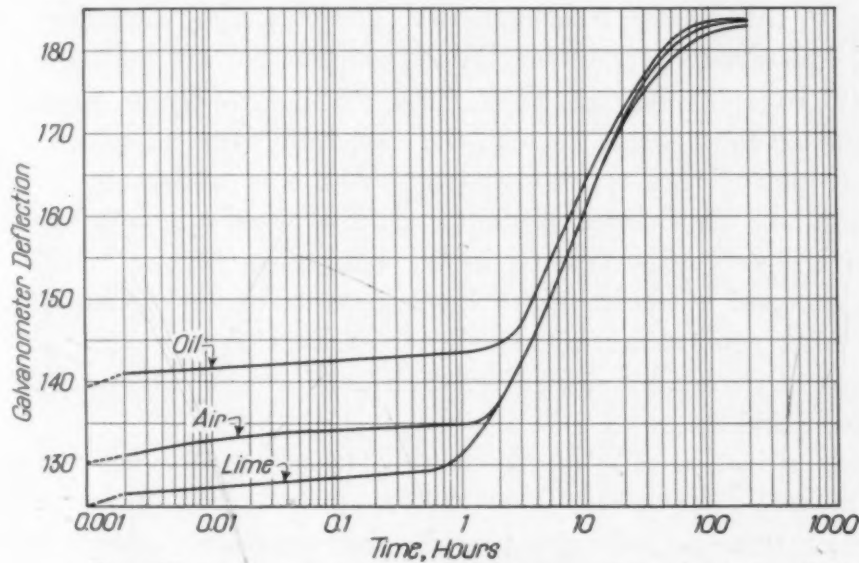


Fig. 4B—Tempering Curves at 900 Degrees Fahr. for 1 Per Cent Carbon—5 Per Cent Chromium Steel Cooled from 1800 Degrees Fahr. as Shown. Measurements at Room Temperature in Field of 770 Gauss.

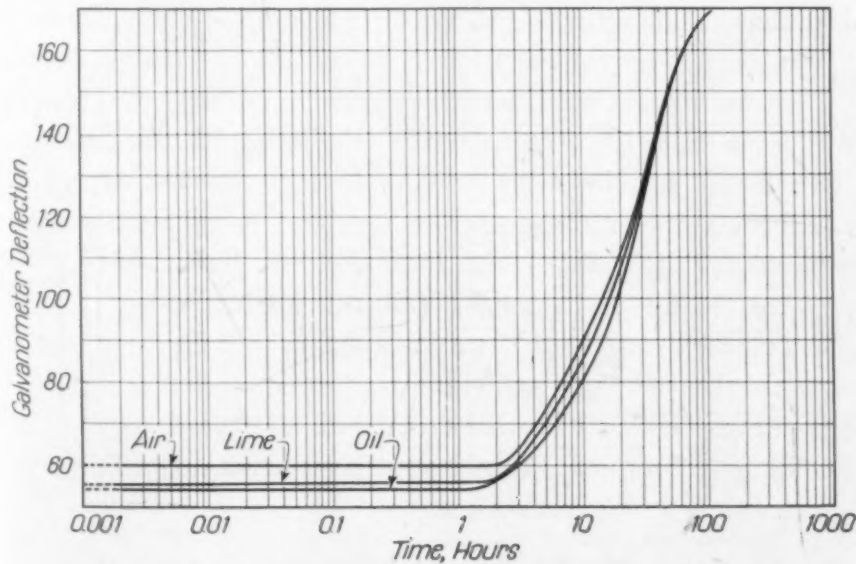


Fig. 4C—Tempering Curves at 900 Degrees Fahr. for 1 Per Cent Carbon—5 Per Cent Chromium Steel Cooled from 2000 Degrees Fahr. as Shown. Measurements Made at Room Temperature in Field of 770 Gauss.

DISCUSSION OF RESULTS

Isothermal Tempering Studies—Before tempering, the amount of retained austenite in the as-hardened steels was determined magnetically by the method of Maurer and Schroeter (12), and the results are shown in Figs. 1 and 2. It must be emphasized that this magnetic method is not rigorous, and the absolute austenite contents indicated in these two figures should only be regarded as to order of magnitude. A much more exact procedure is under development (13). From a comparative point of view, however, it is quite definite that the amount of retained austenite in both steels increases rapidly with the hardening temperature. This is due, of course, to the greater solution of the complex alloy carbides. Figs. 1 and 2 also demonstrate that in the commercial austenitizing range of 1700 to 1900 degrees Fahr. (925 to 1040 degrees Cent.), the retained austenite becomes less, the faster the rate of cooling. Apparently there is an optimum cooling rate for producing the maximum amount of retained austenite after a given austenitizing treatment since very slow cooling in the hardening furnace yields little or no retained austenite. The 1 per cent carbon—5 per cent chromium steel retains more austenite than the 1.5 per cent carbon—12 per cent chromium steel after each hardening treatment indicated in Figs. 1 and 2.

Magnetization-time curves were obtained for twelve tempering temperatures on the two steels after hardening at three temperatures with three quenching rates. Typical curves are shown in Figs. 3 and 4. The increase in magnetization as a result of tempering is associated with the decomposition of the retained austenite; and by assuming that the fractional change in magnetization is proportional to the fraction of the retained austenite which has decomposed, it is possible to construct retained austenite transformation curves as shown in Figs. 5 to 10. These curves demonstrate the time-temperature tempering relationships for achieving the decomposition of various percentages of the austenite retained in the two steels after austenitizing at 1700, 1800 and 2000 degrees Fahr. (825, 980 and 1095 degrees Cent.) and quenching in oil, air and lime.

The retained austenite transformation curves are somewhat analogous to the primary austenite transformation curves, or well-known S-curves, which have been determined for so many steels by hot quenching techniques. However, there are a number of impor-

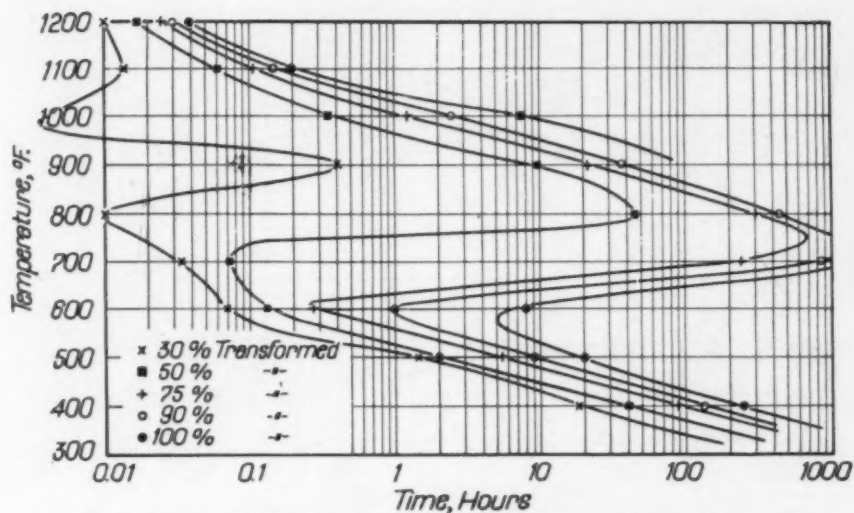


Fig. 5A—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Cooled from 1700 Deg. F.

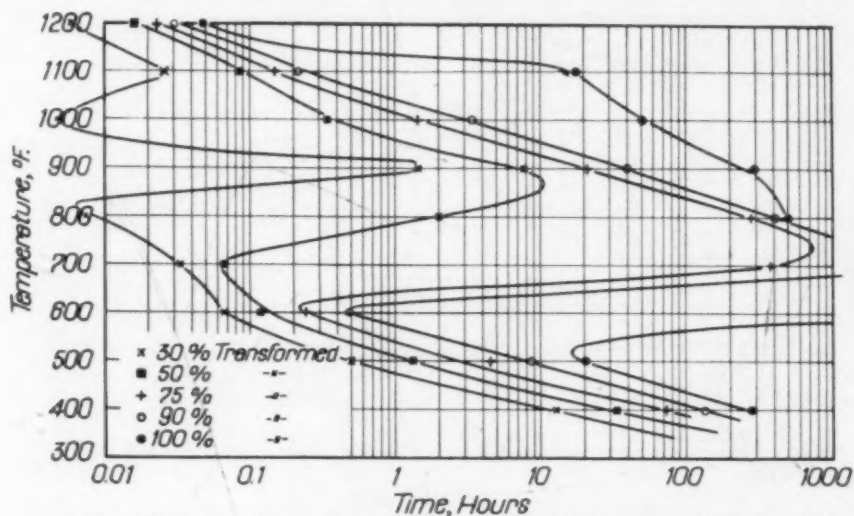


Fig. 5B—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Air-Cooled from 1700 Deg. F.

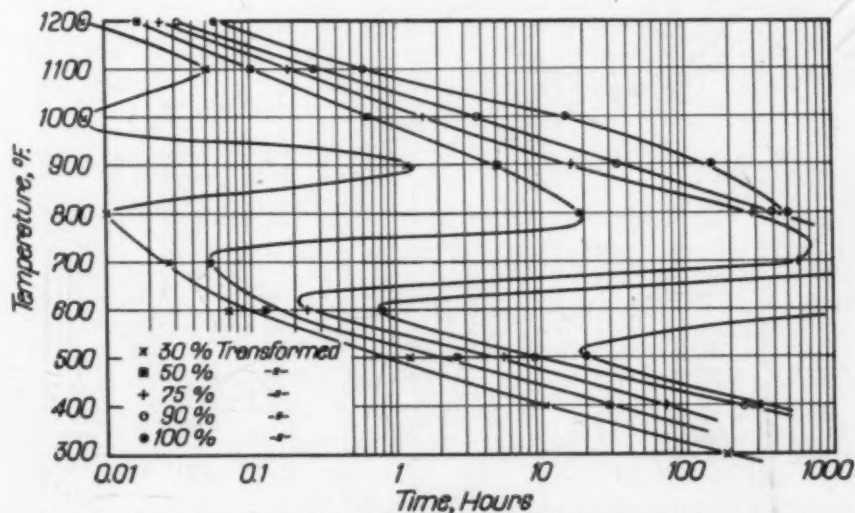


Fig. 5C—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Lime-Cooled from 1700 Deg. F.

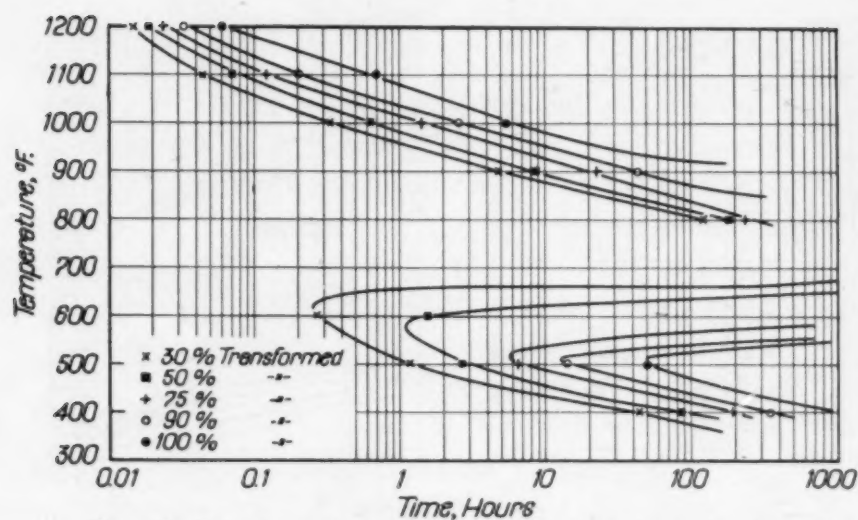


Fig. 6A—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Cooled from 1800 Deg. F.

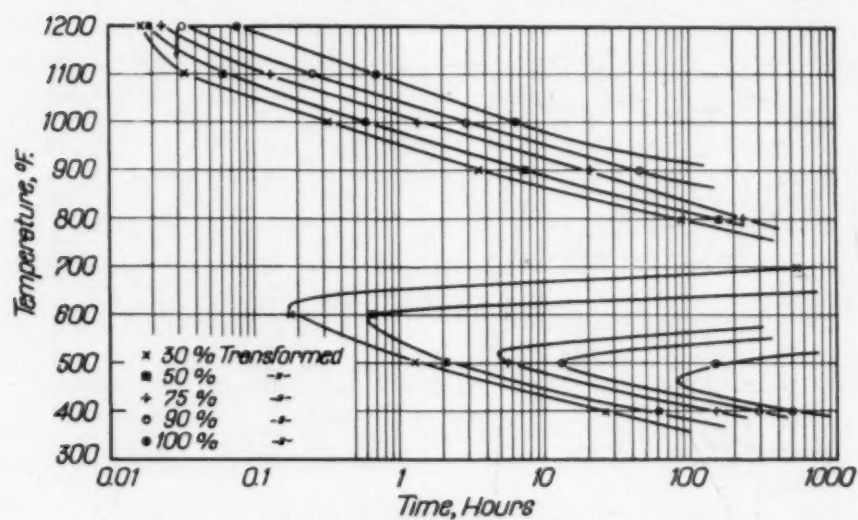


Fig. 6B—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Air-Cooled from 1800 Deg. F.

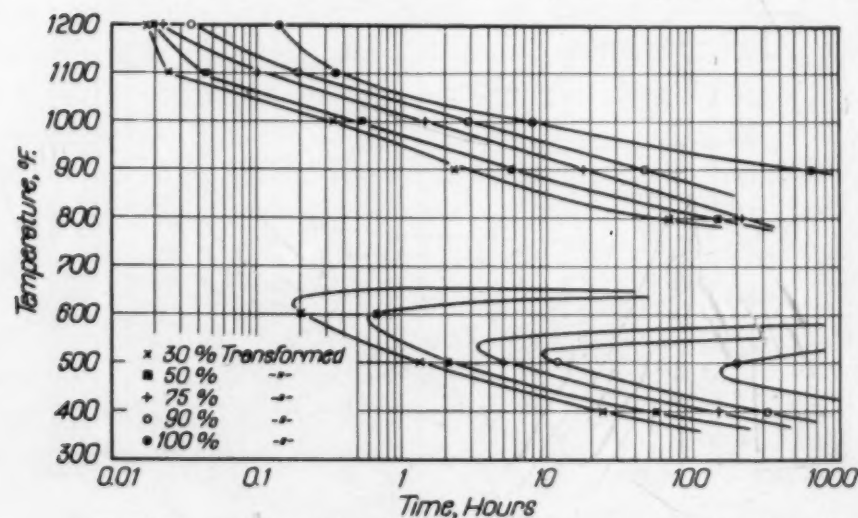


Fig. 6C—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Lime-Cooled from 1800 Deg. F.

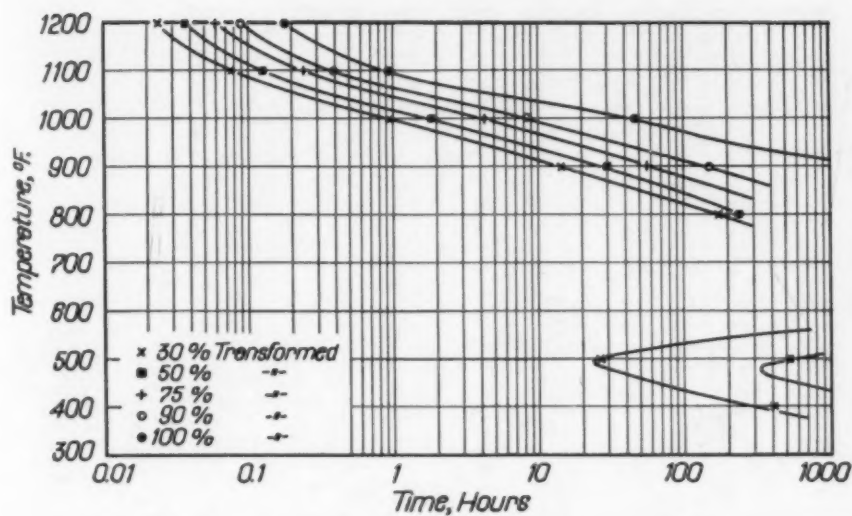


Fig. 7A—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Cooled from 2000 Deg. F.

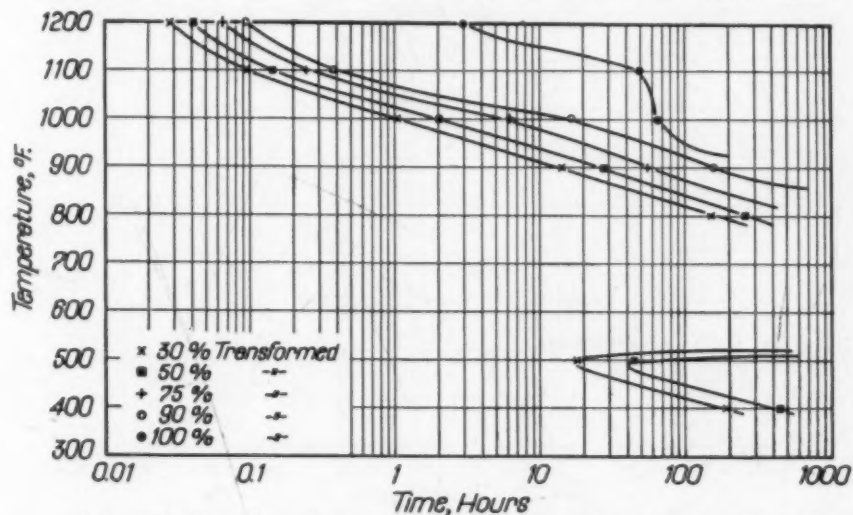


Fig. 7B—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Air-Cooled from 2000 Deg. F.

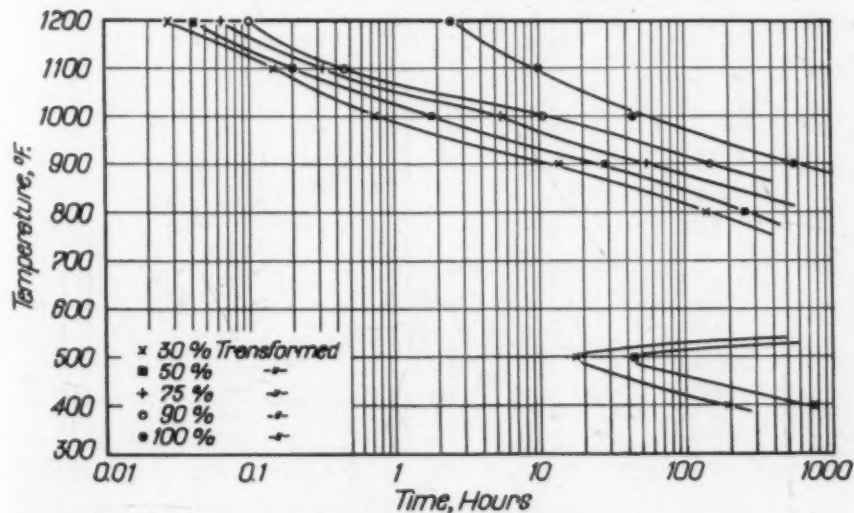


Fig. 7C—Transformation Curves for Retained Austenite in 1 Per Cent Carbon—5 Per Cent Chromium Steel Lime-Cooled from 2000 Deg. F.

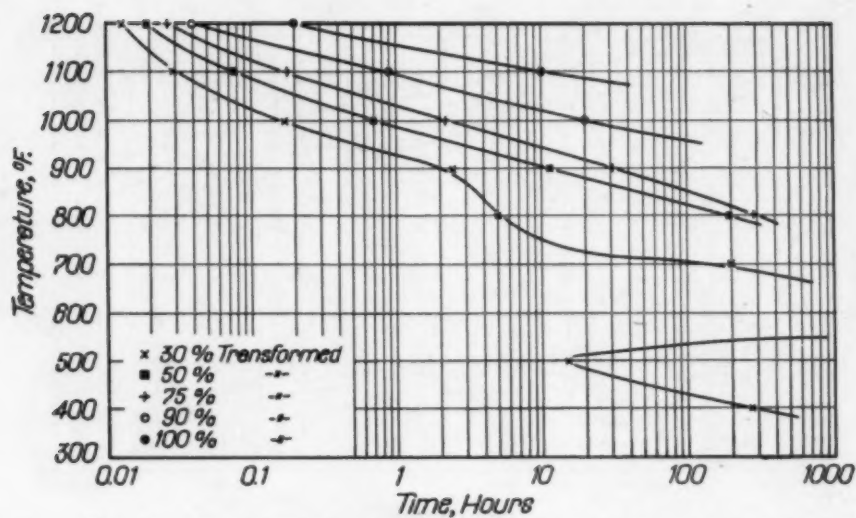


Fig. 8A—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Cooled from 1700 Deg. F.

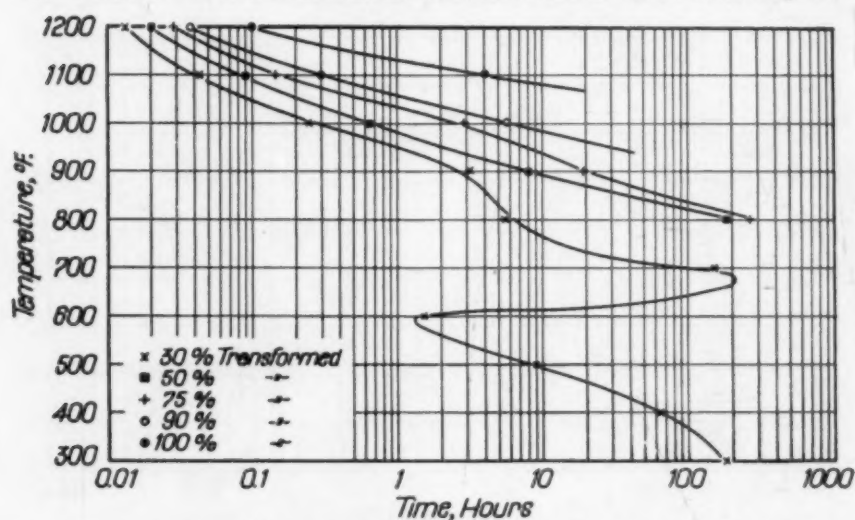


Fig. 8B—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Air-Cooled from 1700 Deg. F.

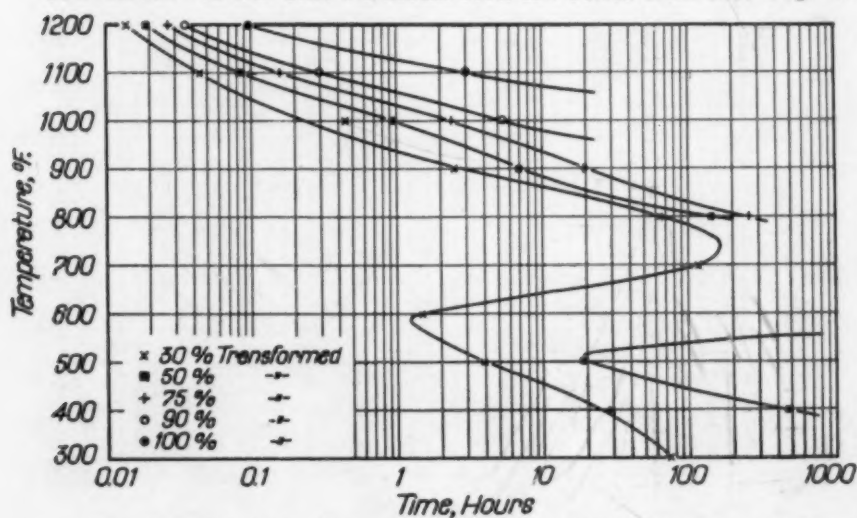


Fig. 8C—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Lime-Cooled from 1700 Deg. F.

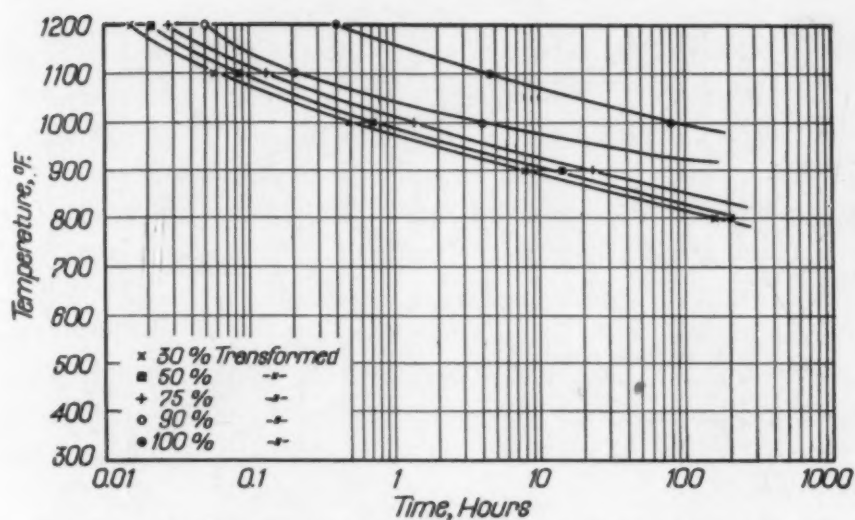


Fig. 9A—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Cooled from 1800 Deg. F.

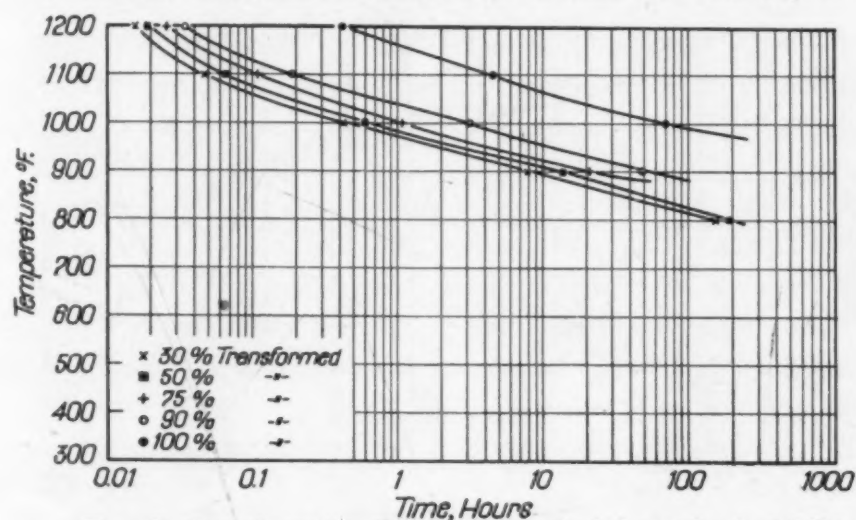


Fig. 9B—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Air-Cooled from 1800 Deg. F.

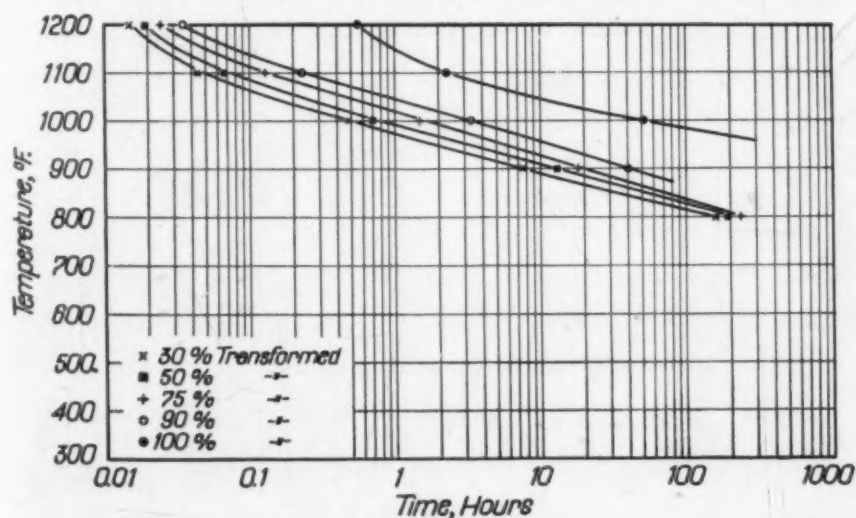


Fig. 9C—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Lime-Cooled from 1800 Deg. F.

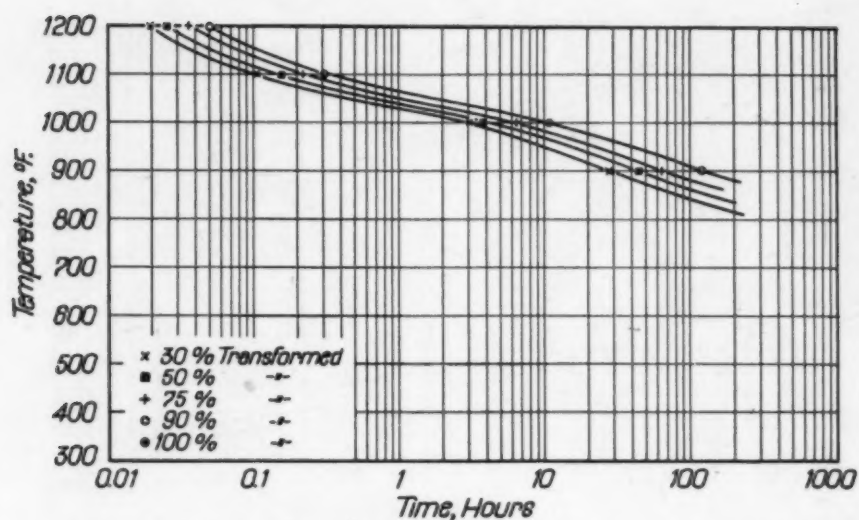


Fig. 10A—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Cooled from 2000 Deg. F.

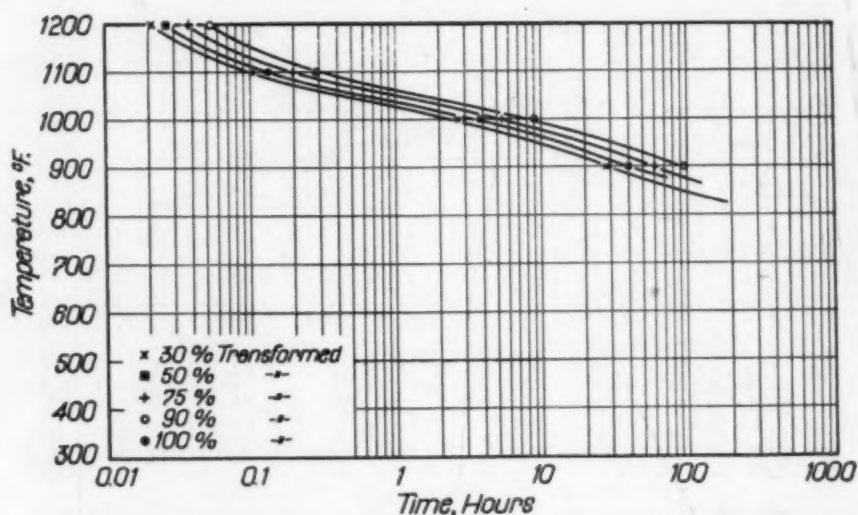


Fig. 10B—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Air-Cooled from 2000 Deg. F.

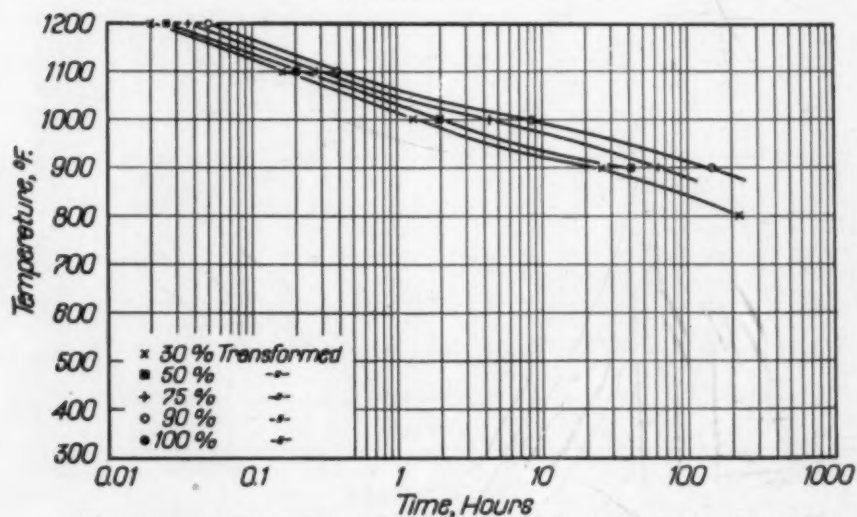


Fig. 10C—Transformation Curves for Retained Austenite in 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Lime-Cooled from 2000 Deg. F.

tant differences. The primary transformation curves indicate the per cent decomposition of all the austenite, while the tempering transformation curves show the per cent decomposition of only the austenite retained in the hardened steel. Moreover, the primary curves trace the austenite decomposition at the holding temperature, whereas the tempering curves in Figs. 5 to 10 depict the austenite decomposition after tempering *and cooling back to room temperature*. Also, in the hardening of steel, the beginnings of the primary transformations are of more consequence than the endings, but in the case of tempering, it is usually the later stages of transformation that are of greater interest (1, 3, 14). This is fortunate since the magnetic method used did not give entirely consistent results during the early stages of retained austenite decomposition. Hence, only the transformation curves above 30 per cent are reproduced in Figs. 5 to 10.

From a comparison of the retained austenite transformation curves, it is evident that the two steels have fundamentally similar tempering characteristics. The 12 per cent chromium steel is much more sluggish than the 5 per cent chromium steel, although the latter contains more austenite in the as-hardened condition. This apparent anomaly is probably due to higher carbon and lower chromium contents dissolved in the austenite of 5 per cent chromium steel than in the 12 per cent chromium steel. Carbon is more potent than chromium in lowering the martensite range on quenching, and hence, in causing more retained austenite; but the chromium is more effective than the carbon in retarding the decomposition of the retained austenite on tempering.

The stability of the retained austenite in the two steels is increased greatly by raising the hardening temperature. Both steels exhibit two temperature ranges of activity: 500 to 600 degrees Fahr. (260 to 315 degrees Cent.) and above 900 degrees Fahr. (480 degrees Cent.). The transformation curves in the lower range are typical C-curves, and are suggestive of bainite formation (15); but in the upper range, the curves are approximately straight as plotted on a logarithmic time scale, and are similar to the straight-line tempering relationships reported for high speed steel (13, 14). The retained austenite in the 12 per cent chromium steel is so sluggish that the C-curves appear only after hardening at 1700 degrees Fahr. (925 degrees Cent.), while in the 5 per cent chromium steel, the low temperature transformation appears even after hardening at 2000 degrees Fahr. (1095 degrees Cent.).

The three different quenching rates from the austenitizing temperature seem to have relatively little effect on the average stability of the retained austenite even though the slower cooling retains more austenite. Thus, large tools which cool rather slowly during air hardening should not require any longer time at the tempering temperature for decomposing a given fraction of the retained austenite than small tools which cool more rapidly and retain less austenite.

Transformations During Heating to and Cooling from the Tempering Temperature—In order to obtain a preliminary survey of the changes which occur during the heating to and cooling from the tempering temperature, seven magnetization-dilation tempering runs were conducted on each of the two steels after oil hardening from temperatures in the range of 1700 to 2200 degrees Fahr. (925 to 1205 degrees Cent.). In each run, the tempering treatment consisted of 2 hours at 1000 degrees Fahr. (540 degrees Cent.) with rates of heating and cooling standardized at 5 degrees Fahr. per minute. To facilitate comparisons, the heating-magnetization, heating-dilation, cooling-magnetization and cooling-dilation curves for each steel are assembled into four sets of plots (Figs. 11 to 14). The positions of the curves relative to one another in these figures have no special significance since they have been displaced vertically to avoid confusing intersections. Isothermal changes at the tempering temperature of 1000 degrees Fahr. (540 degrees Cent.) are not shown; they are generally small compared to the heating and cooling effects.

From the standpoint of this paper, the following features of Figs. 11 to 14 are important:

1. Contractions superimposed upon the normal heating-expansion curves appear in the range of 275 to 375 degrees Fahr. (135 to 190 degrees Cent.) (cf. Figs. 11B and 13B), but with no corresponding change in magnetization (cf. Figs. 11A and 13A). These low temperature contractions disappear after hardening the 1.5 per cent carbon—12 per cent chromium steel from 2050 degrees Fahr. (1120 degrees Cent.) and above. Such high heat treatments result in a nonferromagnetic structure containing no martensite.

2. Contractions superimposed upon the normal heating-expansion curves also appear in the range of 450 to 600 degrees Fahr. (230 to 315 degrees Cent.) (cf. Figs. 11B and 13B), and these changes are attended by drops in magnetization (cf. Figs. 11A and 13A). Again the exceptions to this rule are the curves for the nonmartensitic 1.5 per cent carbon—12 per cent chromium steel after austenitizing above 2050 degrees Fahr. (1120 degrees Cent.).

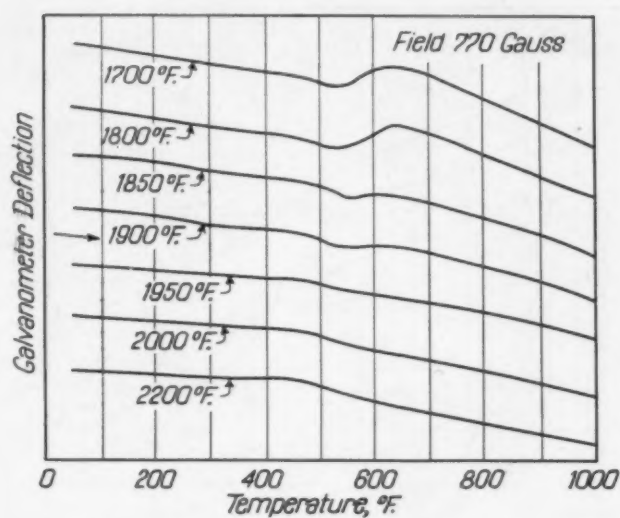


Fig. 11A—Heating-Magnetization Curves of 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown.

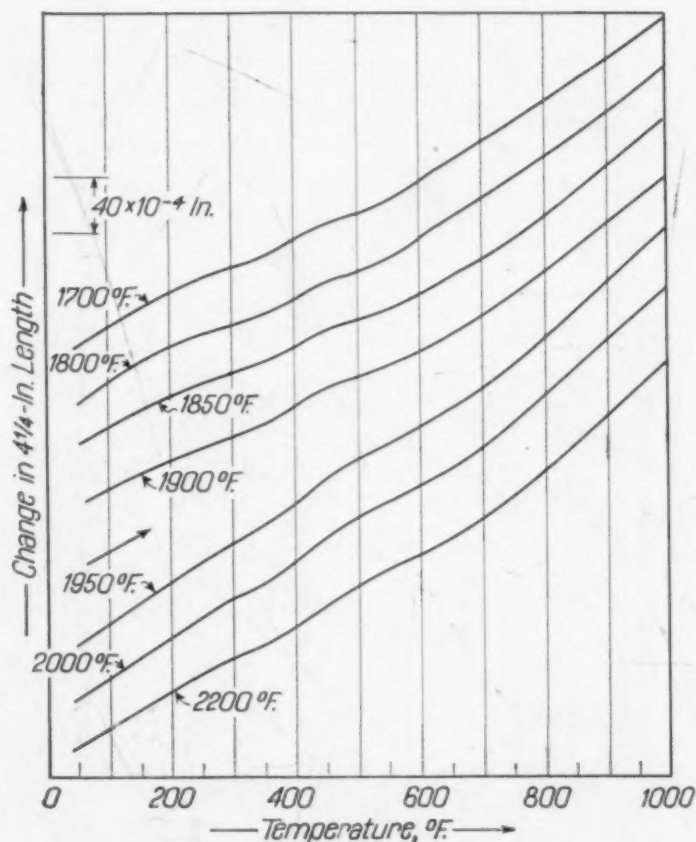


Fig. 11B—Heating-Dilation Curves of 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown.

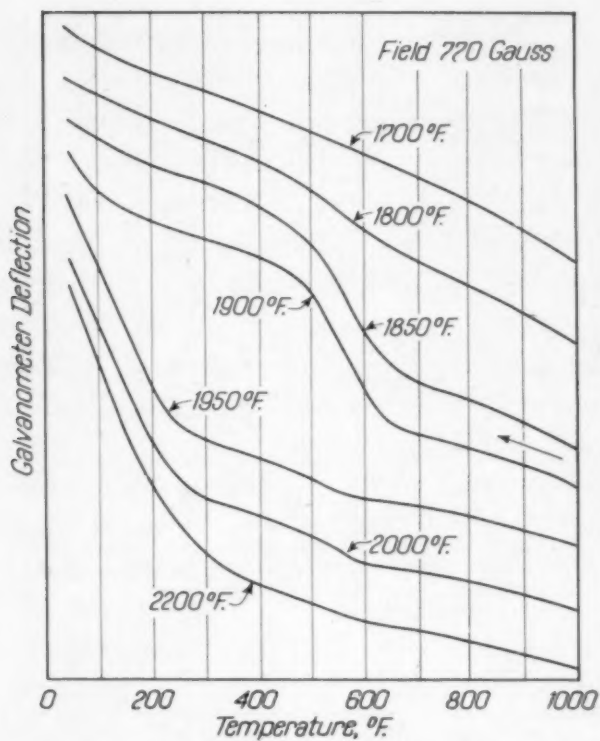


Fig. 12A—Cooling-Magnetization Curves of 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown and Tempered 2 Hours at 1000 Degrees Fahr.

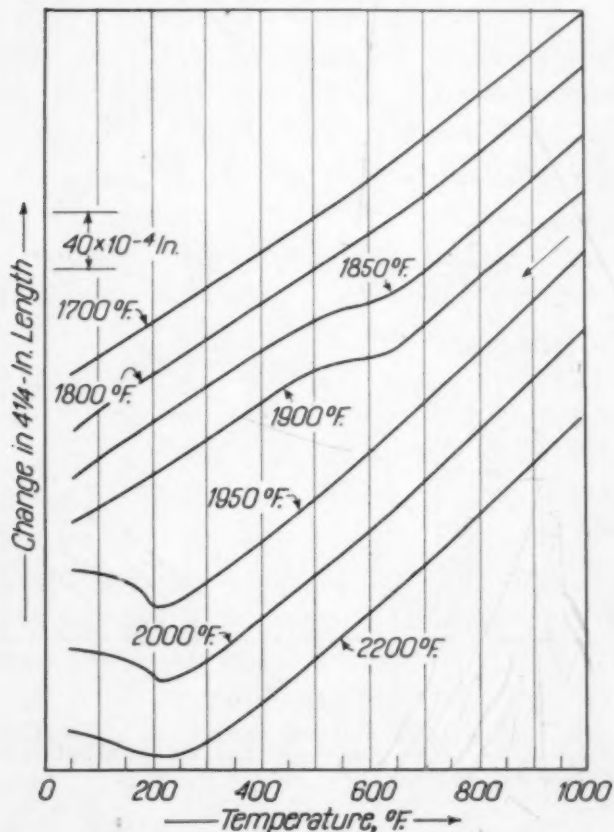


Fig. 12B—Cooling-Dilation Curves of 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown and Tempered 2 Hours at 1000 Degrees Fahr.

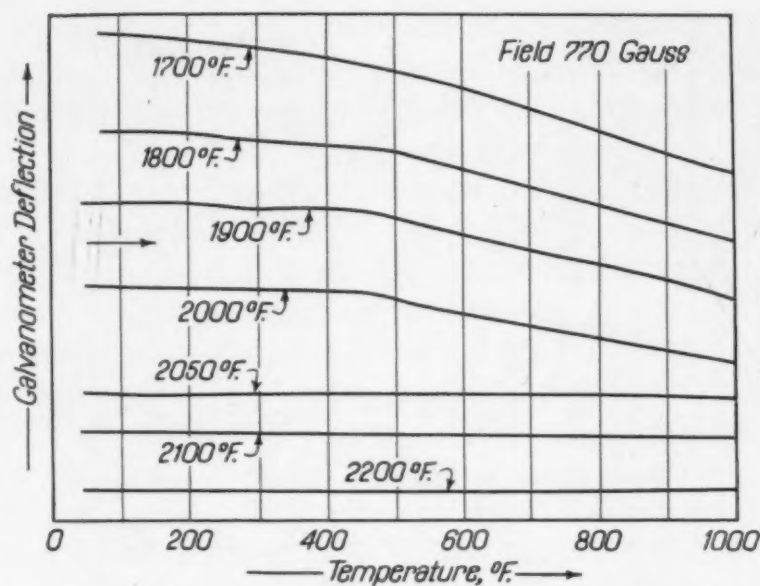


Fig. 13A—Heating-Magnetization Curves of 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown.

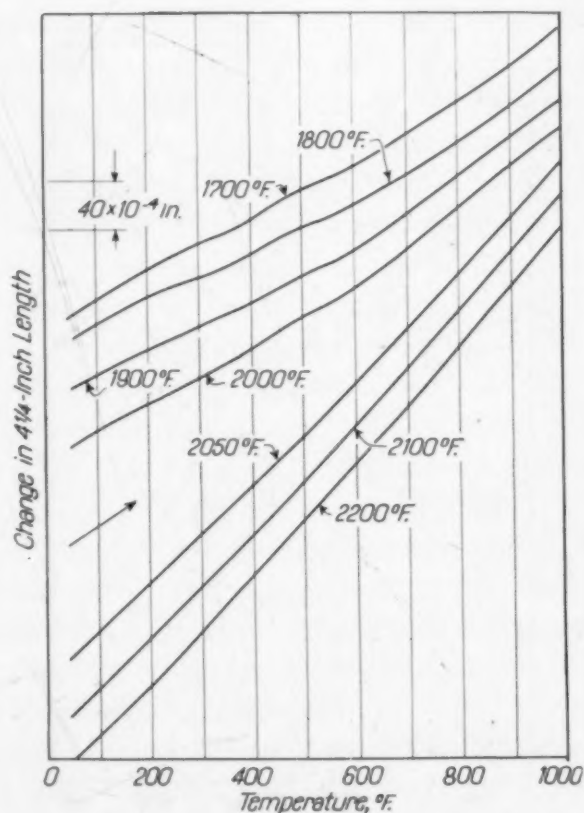


Fig. 13B—Heating-Dilation Curves of 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown.

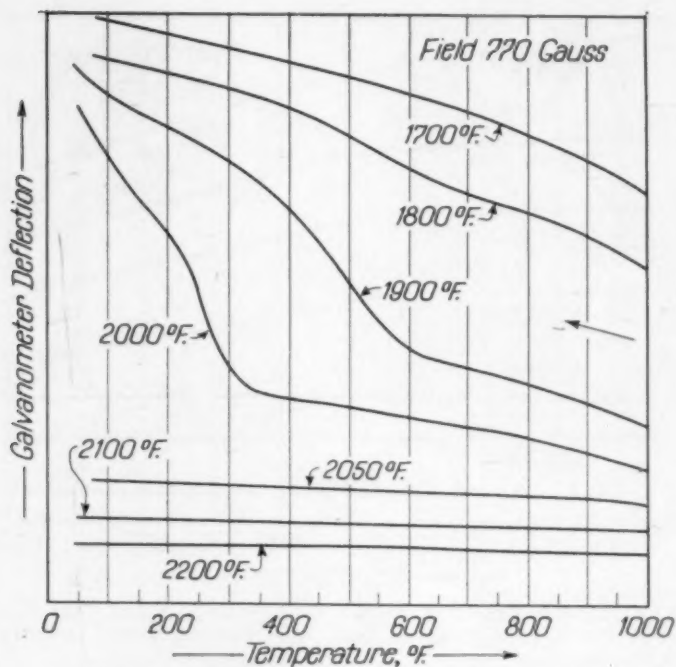


Fig. 14A—Cooling-Magnetization Curves of 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown and Tempered 2 Hours at 1000 Degrees Fahr.

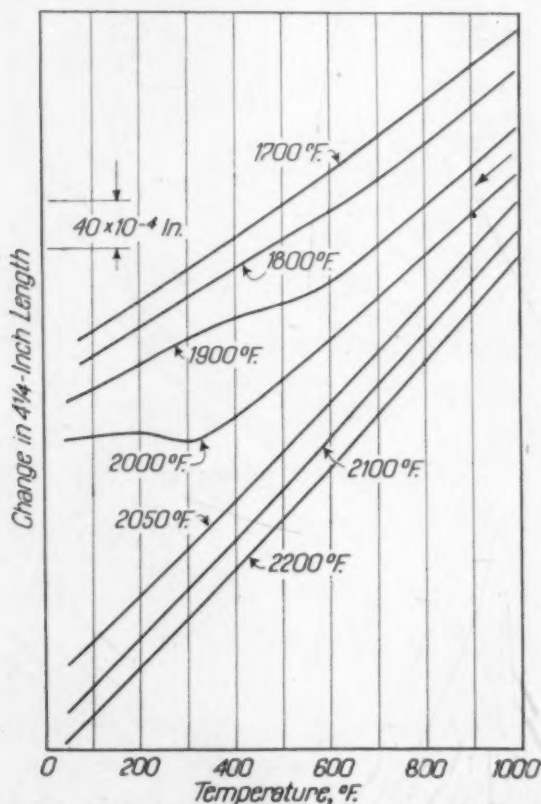


Fig. 14B—Cooling-Dilation Curves of 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Quenched from Temperatures Shown and Tempered 2 Hours at 1000 Degrees Fahr.

3. Retained austenite transformation takes place on heating through the range of 500 to 600 degrees Fahr. (260 to 315 degrees Cent.) in the 1 per cent carbon—5 per cent chromium steel after hardening from temperatures below 1900 degrees Fahr. (1040 degrees Cent.). This transformation is evidenced most clearly by the increase in magnetization which appears in the heating curves of Fig. 11A. There is a corresponding expansion which accompanies this austenite decomposition, but the effect is small, and is barely visible in the heating-dilation curves of Fig. 11B. On austenitizing the 1 per cent carbon—5 per cent chromium steel above 1950 degrees Fahr. (1065 degrees Cent.), however, the retained austenite does not transform during the heating to the tempering temperature. This is also true for the retained austenite in the 1.5 per cent carbon—12 per cent chromium steel after all the hardening treatments.

4. Although not shown directly by Figs. 11 to 14, a small amount of isothermal decomposition occurs during the 2-hour hold at 1000 degrees Fahr. (540 degrees Cent.).

5. Transformation of the retained austenite takes place during the subsequent cooling to room temperature provided that the austenite has not been previously decomposed during the heating and holding, and provided that the austenite is not too stable. The cooling transformation occurs either in the range of 650 to 450 degrees Fahr. (345 to 230 degrees Cent.) or below 300 degrees Fahr. (150 degrees Cent.) or as a split transformation in both ranges. If the retained austenite is comparatively unstable, say after austenitizing the 1 per cent carbon—5 per cent chromium steel at 1700 to 1800 degrees Fahr. (925 to 980 degrees Cent.), all of this austenite decomposes during the heating to and holding at the tempering temperature, and hence none is available for transformation during the subsequent cooling (cf. Figs. 12A and 12B). After hardening this steel at 1850 degrees Fahr. (1010 degrees Cent.), the retained austenite transforms both during heating and during cooling. With still higher hardening temperatures, the heating transformation vanishes, and the cooling transformation splits into the two-step process mentioned above. On austenitizing above 1950 degrees Fahr. (1065 degrees Cent.), the transformation in the lower step increases while the upper step gradually disappears. The same story holds in a general way for the 1.5 per cent carbon—12 per cent chromium steel (cf. Figs. 14A and 14B). In the latter case, however, the retained austenite produced by hardening above 2050 degrees Fahr. (1120 de-

degrees Cent.) is too sluggish to transform at all even during the lower step of the split transformation range.

It is worth repeating here that the above statements are based on oil-quenched specimens, a single tempering treatment of 2 hours at 1000 degrees Fahr. (540 degrees Cent.), and arbitrary heating and cooling rates of 5 degrees Fahr. per minute. Consequently, experiments were instituted to explore the effects of varying these factors.

Fig. 15 shows two sets of magnetization heating and cooling curves (constant rate of 5 degrees Fahr. per minute) for the 1 per cent carbon—5 per cent chromium steel subjected to a given tempering treatment after three quenching rates from a hardening temperature of 1800 degrees Fahr. (980 degrees Cent.). The magnetic measurements were made at two field strengths of 265 and 1000 gauss for reasons to be discussed later. The curves in Fig. 15 are plotted in their true relative positions, unlike the previous magnetization curves. Hence, the extent of isothermal transformation at 1000 degrees Fahr. (540 degrees Cent.) is indicated by the displacement between the corresponding heating and cooling curves. It is also clear that the faster quenches produce higher magnetization values in the as-hardened condition, thus signifying less retained austenite. The amount of isothermal transformation is not appreciably influenced by the quenching rate from the austenitizing temperature. However, the heating and cooling transformations increase in magnitude as the rate of the hardening quench is decreased so that, by the time the specimens reach room temperature after the tempering, the retained austenite is completely decomposed despite the different amounts originally present in the three as-hardened states. These observations are in line with the room temperature measurements described on page 394.

The retained austenite transformations in Fig. 15 are attended by increases in magnetization at both the high and low field strengths, as is to be expected. However, during the heating, before the austenite begins to decompose, there is an increase in magnetization in the range of 300 to 450 degrees Fahr. (150 to 230 degrees Cent.) as measured at the low field, but there is no corresponding increase at the high field. This effect of field dependence was verified by many other runs, and has been shown to be due to stress relief (16-18).

The retained austenite transformation during heating to the tem-

pering temperature is a time-dependent process, and continues if the heating is stopped in the reactive range of 500 to 600 degrees Fahr. (260 to 315 degrees Cent.). By the same token, rapid heating through this range inhibits the heating transformation, and makes more austenite available for isothermal decomposition at the tempering temperature and for further decomposition during the subsequent cooling. It is important to note that this reactive range corresponds to the C-curve temperatures on the tempering transformation curves developed by room temperature measurements (cf. Fig. 6). Furthermore, the first step of the split transformation on cooling occurs over the same temperature range. The austenite decomposition in the first step of the cooling transformation can be suppressed by rapid cooling from the tempering temperature, and hence is likewise a time-dependent process. It may be safely assumed, therefore, that the decomposition product is the same in this range whether it forms isothermally or during heating or during cooling. As shown by recent studies on the kinetics of austenite decomposition in high speed steel (15), these transformation characteristics are indicative of bainite formation. When such bainite formation is avoided by rapid cooling, the austenite decomposes during the second step of the split transformation. The second step does not appear to be suppressible by rapid cooling, which suggests a transformation of the retained austenite into martensite (15). This was confirmed by X-ray measurements (page 404).

The retained austenite is quite sluggish in the range from 700 to 800 degrees Fahr. (370 to 425 degrees Cent.), but on tempering at higher temperatures, the austenite becomes conditioned for transformation during the subsequent cooling, as in the case of high speed steel (1). Moreover, isothermal transformation during tempering becomes more important as the tempering temperatures and times are increased. These effects are shown by the magnetization curves in Fig. 16 after hardening 1 per cent carbon—5 per cent chromium steel at 2000 degrees Fahr. (1095 degrees Cent.). Comparing the cooling curves 2, 3 and 4, it is evident that tempering above 900 degrees Fahr. (480 degrees Cent.) first conditions the retained austenite for transformation into martensite during the cooling. With increased tempering temperature and time, the cooling transformation splits and bainite forms at the expense of the martensite. However, as the tempering exposure is still further increased, extensive isothermal decomposition sets in and leaves correspondingly less

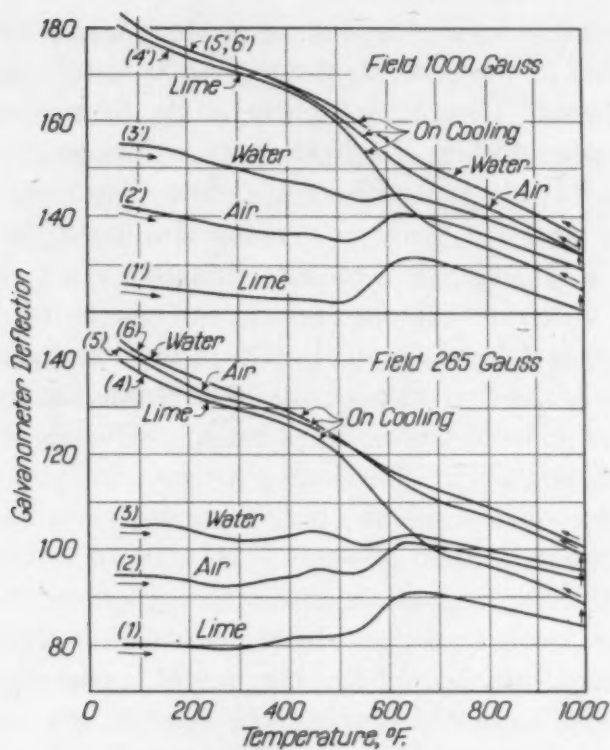


Fig. 15—Heating and Cooling Magnetization Curves for 1 Per Cent Carbon—5 Per Cent Chromium Steel. Austenitized at 1800 Degrees Fahr. and Cooled as Shown. Holding Time at 1000 Degrees Fahr. = 2 Hours.

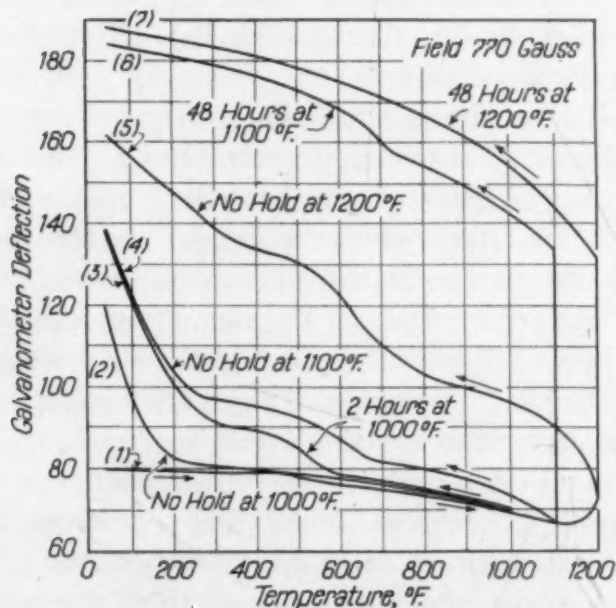


Fig. 16—Magnetization Curves Showing Effects of Tempering Time and Temperature on the Isothermal and Cooling Transformations of the Retained Austenite in the 1 Per Cent Carbon—5 Per Cent Chromium Steel. Oil-Quenched from 2000 Degrees Fahr.

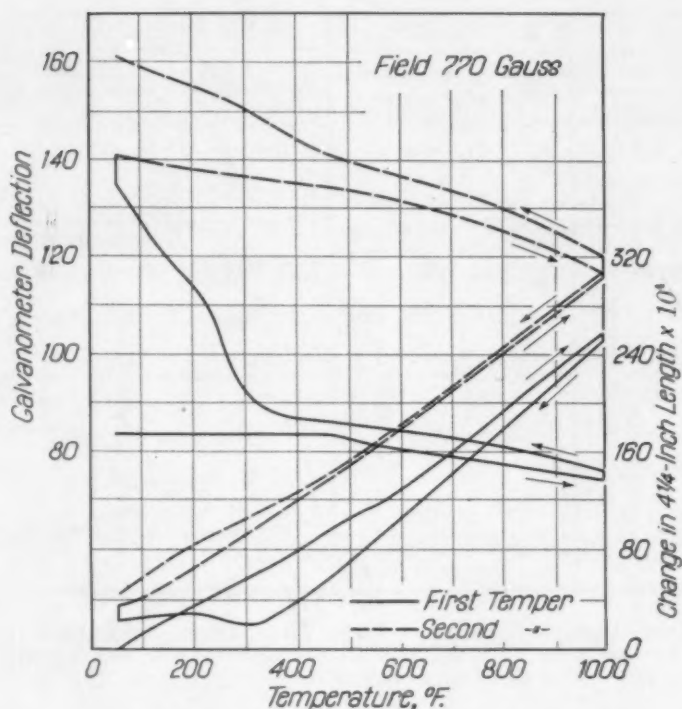


Fig. 17—Magnetization and Dilation Changes During a Double Tempering Run on the 1.5 Per Cent Carbon—12 Per Cent Chromium Steel Oil-Quenched from 2000 Degrees Fahr. Holding Time at 1000 Degrees Fahr. = 2 Hours.

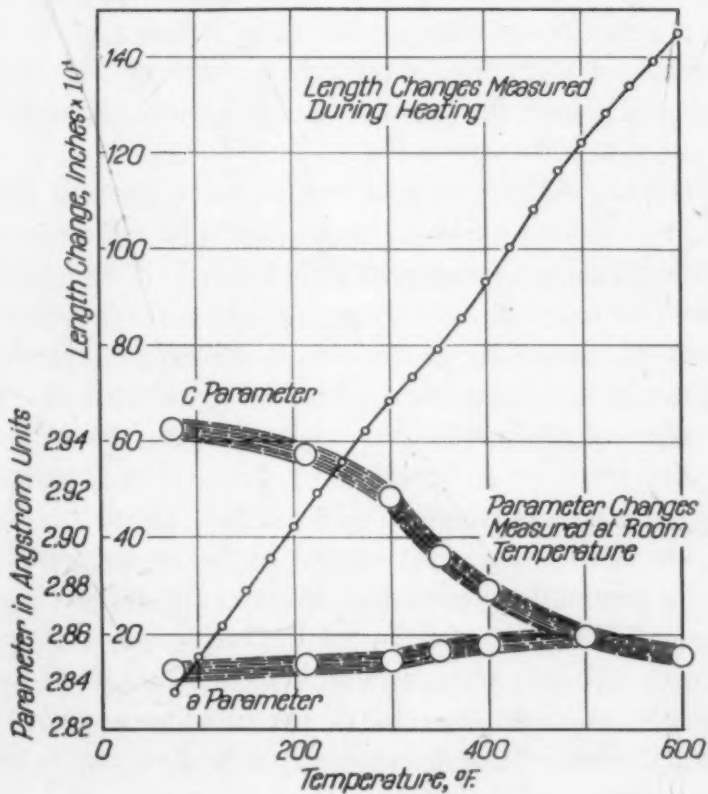


Fig. 18—Parameter and Length Changes in a 1 Per Cent Carbon—5 Per Cent Chromium Steel Oil-Quenched from 2000 Degrees Fahr. and Tempered for $\frac{1}{2}$ Hour as Shown.

to carbide precipitation from the tempered martensite. This carbide precipitation also explains the accompanying decrease in magnetization (cf. item 2) since the carbide phase is nonferromagnetic. The details of these stages in the tempering of martensite are now being studied on less complicated steels.

The decomposition of the retained austenite as a result of tempering was followed qualitatively by observing the decreasing density of the austenite diffraction lines relative to the density of a reference line obtained by exposing an aluminum filter simultaneously with the specimen (19). Reasonably good agreement with the magnetic measurements was found. The microphotometer traces in Fig. 19 are particularly instructive. There is little change in the density of the austenite lines after tempering for 0.5 hour at 400 degrees Fahr. (205 degrees Cent.), but the tetragonal doublet of the primary martensite merges into a single line. After further tempering at 980 degrees Fahr. (525 degrees Cent.) for 100 hours, however, the austenite lines diminish markedly in intensity, and the martensite doublet reappears. This is due to the transformation of the retained austenite into secondary martensite on cooling from the tempering treatment. By tempering once more at 400 degrees Fahr. (205 degrees Cent.), the tetragonal structure decomposes, and the doublet merges into a single line again.

CONCLUSIONS

1. The tempering characteristics of 1 per cent carbon—5 per cent chromium and 1.5 per cent carbon—12 per cent chromium steels are similar in principle. The tempering mechanism is somewhat more complicated than that of high speed steel since a wider range of retained austenite contents and stabilities can be obtained in the high-carbon high-chromium series. The amount of retained austenite and its stability are greater, the higher the hardening temperature.

2. Oil, air and lime cooling from temperatures in the commercial austenitizing range produces increasing amounts of retained austenite in the order named. However, no austenite is retained on furnace cooling.

3. For a given hardening treatment in this range, there is more retained austenite in the 1 per cent carbon—5 per cent chromium steel than in the 1.5 per cent carbon—12 per cent chromium

steel, but the stability of the austenite in the latter is greater than in the former.

4. The kinetics of the retained austenite decomposition as a result of tempering are shown in the form of transformation curves. The retained austenite in the 1 per cent carbon—5 per cent chromium steel undergoes rapid isothermal transformation in the range of 500 to 600 degrees Fahr. (260 to 315 degrees Cent.), particularly if hardened below 1800 degrees Fahr. (980 degrees Cent.). The product is undoubtedly bainite. The 1.5 per cent carbon—12 per cent chromium steel shows some activity in this range, but only if hardened at the low temperature of 1700 degrees Fahr.

5. The retained austenite in both steels is very sluggish in the range of 700 to 800 degrees Fahr. (370 to 425 degrees Cent.). On tempering above 900 degrees Fahr. (480 degrees Cent.), the austenite becomes conditioned for transformation during subsequent cooling. At 1100 degrees Fahr. (595 degrees Cent.) or above, the austenite decomposes isothermally, and leaves less available for the cooling transformation.

6. The cooling transformation after tempering occurs either in the range of 650 to 450 degrees Fahr. (345 to 230 degrees Cent.) into bainite or below 300 degrees Fahr. (150 degrees Cent.) into tetragonal martensite. With certain combinations of hardening and tempering, the cooling transformation splits into two steps, taking place partly in each of the above ranges. The bainite formation can be suppressed by rapid cooling, thus resulting in more martensite. For a given rate of cooling, however, high temperatures and long times of tempering promote the formation of bainite at the expense of martensite during cooling.

7. During the heating of the hardened steel, the primary martensite changes from tetragonal to cubic in the range of 200 to 500 degrees Fahr. (95 to 260 degrees Cent.). This process is overlapped by stress relief. Evidence of carbide precipitation from the tempered martensite is found in the range of 450 to 600 degrees Fahr. (230 to 315 degrees Cent.).

8. Depending upon the hardening and tempering conditions, the retained austenite can be made to transform during the heating to, the holding at, or the cooling from the tempering temperature. For a given tempering treatment, the relative and absolute amounts of retained austenite which decompose during these stages are controlled by the austenitizing treatment.

ACKNOWLEDGMENTS

The authors desire to acknowledge their indebtedness to N. I. Stotz of the Universal-Cyclops Steel Corporation for the steel and the chemical analyses; to John Paine of the United Shoe Machinery Corporation for the centerless grinding of the rod stock; and to L. H. Penn, D. P. Antia, J. Connelly, and H. Rahman for valuable aid in the preparation of the manuscript.

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DISCUSSION

Written Discussion: By Dara P. Antia, Massachusetts Institute of Technology, Cambridge, Mass.

This is the first paper to present retained austenite transformation curves which are analogous to the familiar isothermal (or S-curves), and we now have an opportunity to compare directly the kinetics of the primary austenite and the retained austenite transformations.

Accordingly, the primary transformation curves were determined for the two high-carbon, high-chromium steels used in the authors' tempering studies. The hot quenching experiments were conducted according to the metallographic techniques of Davenport-Bain and Greninger-Troiano on specimens $\frac{1}{8}$ inch in diameter by $\frac{1}{8}$ inch long. In the latter procedure, a treatment of 10 seconds at 1000 degrees Fahr. (540 degrees Cent.) followed by quenching in water was adopted for darkening the primary transformation products. The transformation curves shown in Figs. A and B were established for an austenitizing temperature of 1800 degrees Fahr. (980 degrees Cent.) and should therefore be compared to Figs. 6 and 9 of the paper.

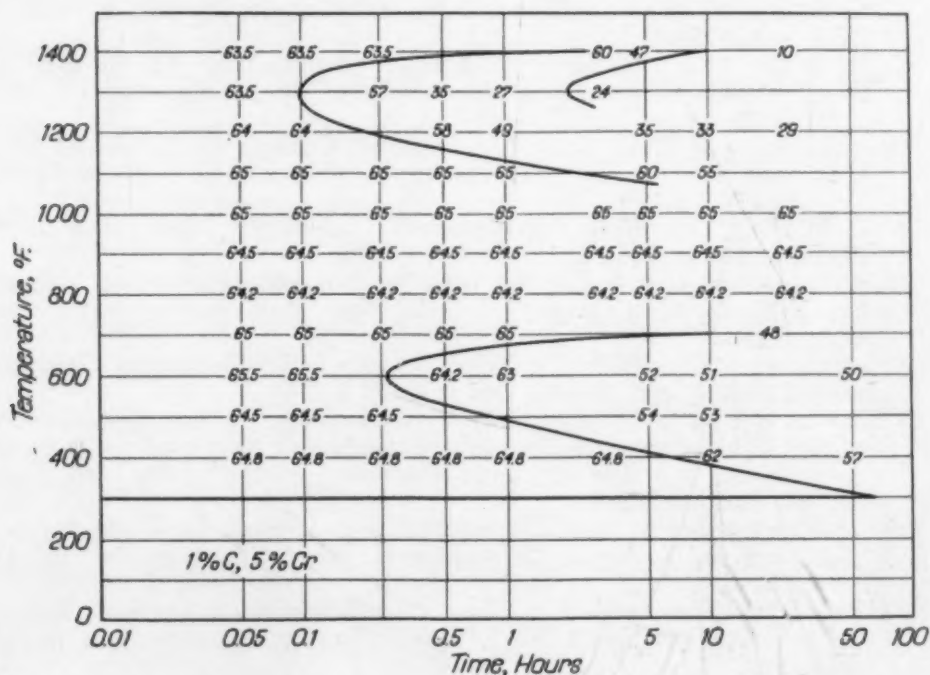


Fig. A—Primary Transformation Curves for 1 Per Cent Carbon, 5 Per Cent Chromium Steel Hot Quenched from 1800 Degrees Fahr. Numbers Show Rockwell C Hardness Values After Indicated Treatments and Water Quenching to Room Temperature.

The primary transformation curves for the two chromium steels are very similar, having two regions of isothermal activity at about the same temperature ranges. These ranges also correspond to the tempering temperatures at which the retained austenite undergoes relatively rapid decomposition (cf.

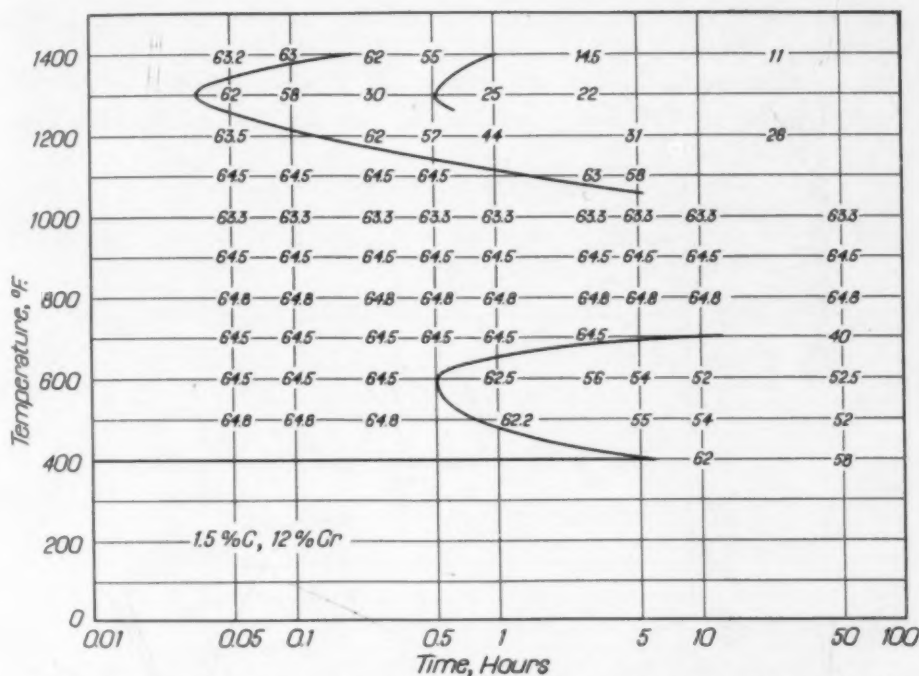


Fig. B—Primary Transformation Curves for 1.5 Per Cent Carbon, 12 Per Cent Chromium Steel Hot Quenched from 1800 Degrees Fahr. Numbers Show Rockwell C Hardness Values After Indicated Treatment and Water Quenching to Room Temperature.

authors' conclusions). In addition, it is quite likely that the products of isothermal decomposition during tempering are the same as the products of isothermal decomposition during hot quenching.

However, there are important differences in detail between the primary and secondary transformation characteristics. This must be expected since the regular S-curves depict the decomposition of the whole austenitized structure, while the tempering curves deal with only the austenite which remains after the steel has been directly cooled through the martensitic range to room temperature. In the range of 400 to 700 degrees Fahr. (205 to 370 degrees Cent.), the retained austenite transforms rather slowly compared to the rate of primary transformation at these temperatures. On the other hand, above 800 degrees Fahr. (425 degrees Cent.), the retained austenite transformation goes to completion much more quickly than the primary transformation. Consequently, the bays of the two types of transformation curves do not coincide, although both the primary and retained austenites have temperature ranges of great sluggishness. These differences in detail demonstrate quite clearly that any attempt to use hot quenching data for ascertaining the time-temperature combinations for attaining complete transformation of the retained austenite (or for avoiding transformation of the retained austenite) is open to serious question. At

the same time, it appears that the basic tendencies which govern the primary transformation of austenite are also at play during the tempering of retained austenite.

Written Discussion: By Robert T. Howard, Massachusetts Institute of Technology, Cambridge, Mass.

The authors have focussed attention on the transformations which occur during the tempering of two important high-chromium steels. In cooperation with the authors and as a part of a Bachelor's thesis conducted at the Massachusetts Institute of Technology, the writer studied the relationship between

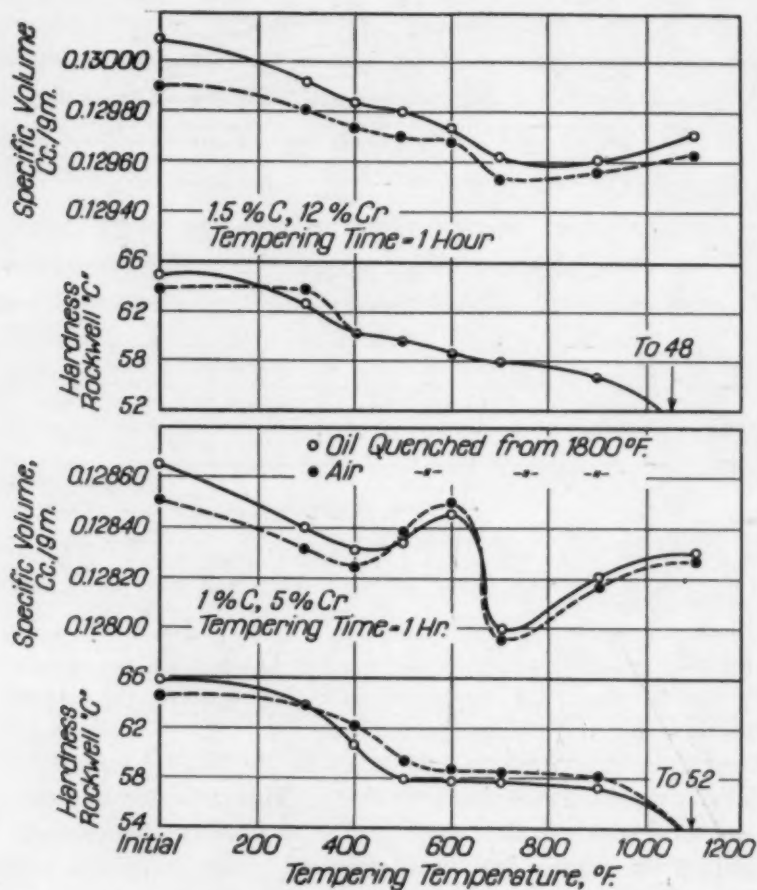


Fig. C—Tempering Curves for High-Carbon, High-Chromium Steels.

these tempering transformations and the simultaneous hardness changes. Such an investigation was considered desirable since much of the past work on these steels has been based on hardness determinations.

Half-inch cubes of the very same two steels used by Zmeskal and Cohen were hardened by quenching in oil and in air from 1800 degrees Fahr. (980 degrees Cent.). These specimens were then tempered in liquid baths for cumulative times of 0, 0.02, 0.10, 1.0, 2.5, 10.0 and 100.0 hours at temperatures of 400, 500, 600, 700, 900 and 1100 degrees Fahr. (205, 260, 315, 370, 480 and 595 degrees Cent.). After each tempering treatment the Rockwell C hardness and specific volume were carefully measured. Isothermal tempering curves were

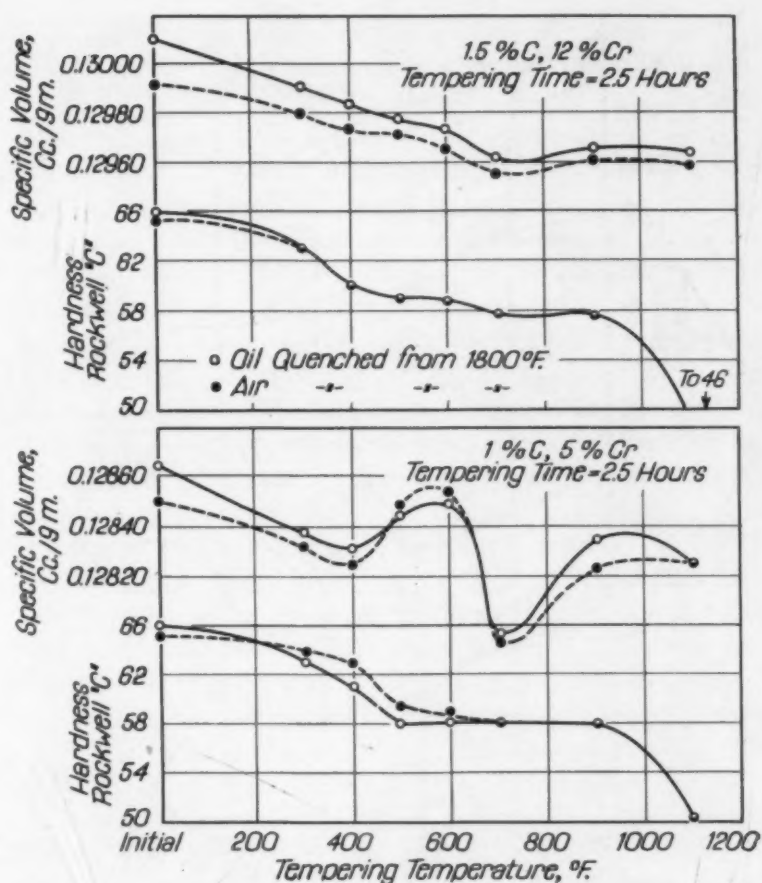


Fig. D—Tempering Curves for High-Carbon, High-Chromium Steels.

plotted for each of the above temperatures, but in order to conserve space here, summarizing curves are given in Figs. C, D, and E for tempering times of 1.0, 2.5 and 10.0 hours only. It may be stated, however, that the course of retained austenite transformation as revealed magnetically in Figs. 6A, 6B, 9A and 9B was reasonably well substantiated by the specific volume measurements. In general, it appears that the specific volume method for studying retained austenite decomposition is not nearly as sensitive as the magnetic technique employed by the authors, but on the other hand, the magnetic measurements are more easily affected by extraneous factors and require great care in interpretation.

As indicated in Figs. C, D and E, the specific volume and hardness values of the as-hardened steels are greater after oil quenching than after air cooling. This confirms the authors' findings that more austenite is retained with the slower rate of cooling. On tempering, however, the oil and air cooling data tend to converge in agreement with the authors' statement "Different quenching rates from the austenitizing temperature seem to have little effect on the average stability of the retained austenite, even though the slower cooling retains more austenite."

The rapid decomposition of the retained austenite in the 1 per cent carbon-5 per cent chromium steel on tempering in the range of 500 to 600 degrees

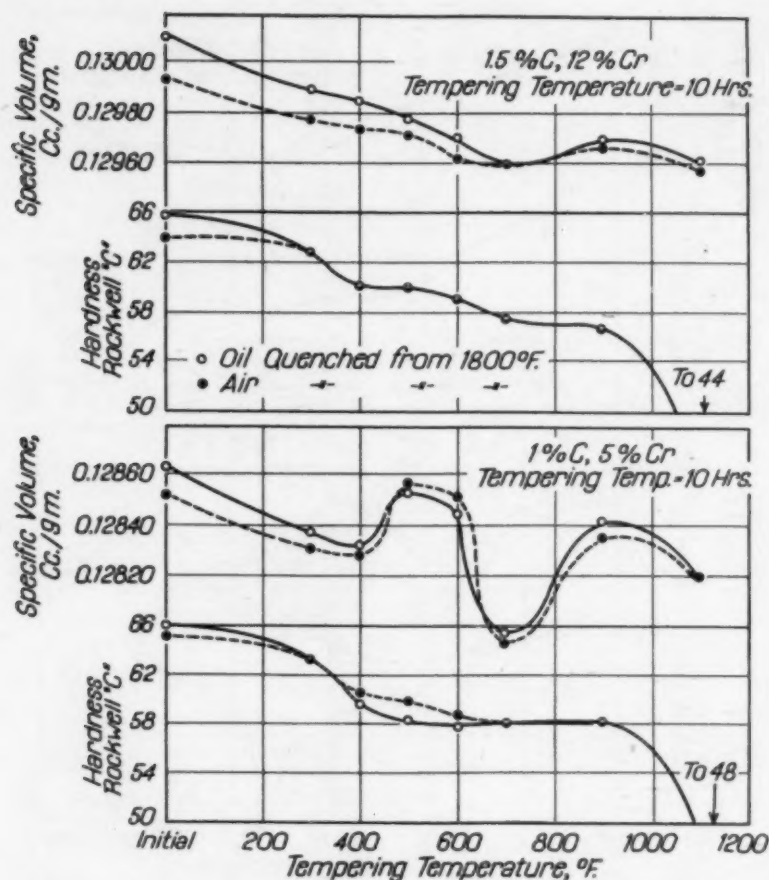


Fig. E—Tempering Curves for High-Carbon, High-Chromium Steels.

Fahr. (260 to 315 degrees Cent.) is strikingly demonstrated by the hump in the specific volume curves. At 700 degrees Fahr. (370 degrees Cent.), the retained austenite becomes very sluggish, and above 800 degrees Fahr. (425 degrees Cent.), the increasing specific volume signifies that the austenite becomes reactive again. (It should be emphasized that in studying these higher tempering temperatures, the specimens were heated rapidly enough so that the retained austenite did not have an opportunity to transform in the range of 500 to 600 degrees Fahr.). In the case of the 1.5 per cent carbon-12 per cent chromium steel, there is little, if any, austenite transformation in this low temperature range, but above 800 degrees Fahr. (425 degrees Cent.) the specific volume curves show definite evidence of austenite transformation in accordance with the authors' magnetic and dilatometric measurements.

The initial softening of these steels during tempering coincides with a decrease in the specific volume, and is, therefore, attributable to the decomposition of the tetragonal martensite. Above 400 to 500 degrees Fahr. (205 to 260 degrees Cent.), the hardness remains fairly constant, even when the tempering temperature approaches 900 degrees Fahr. (480 degrees Cent.). This "plateau" extends well beyond the 500 to 600 degrees Fahr. (260 to 315 degrees Cent.) range of retained austenite decomposition in the 1 per cent carbon-5 per cent chromium steel, and cannot be due to the latter transformation.

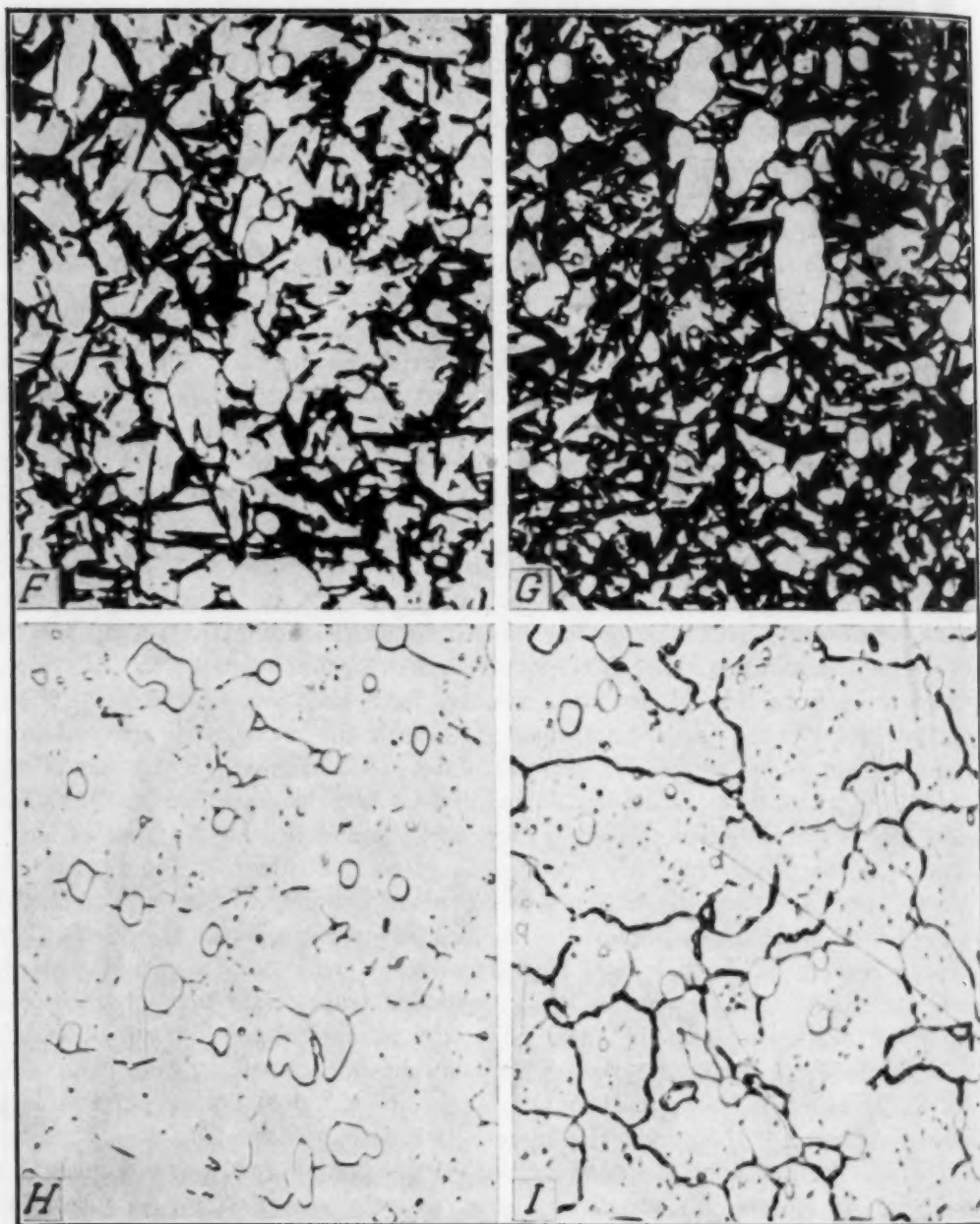
Furthermore, in the 1.5 per cent carbon-12 per cent chromium steel, there is no significant amount of austenite decomposition in this range, and yet the hardness curve flattens out in a manner similar to that of the 1 per cent carbon-5 per cent chromium steel. It is evident that the retarded softening above 400 to 500 degrees Fahr. (205 to 260 degrees Cent.) in these high-carbon, high-chromium steels cannot be ascribed to the transformation of the retained austenite. More likely, the retarded softening is caused by a precipitation of carbides from the tempered martensitic matrix, which offsets the softening usually encountered in less highly alloyed steels. These carbides are believed to be rich in chromium since, unlike cementite, they are nonferromagnetic at room temperature. This precipitation seems to be identical with that postulated by the authors on page 404. The second decrease in specific volume in the 1.5 per cent carbon-12 per cent chromium steel is also evidence of this precipitation process. In the 1 per cent carbon-5 per cent chromium steel, this contraction is obscured by the large expansion due to the austenite transformation.

On tempering above 800 degrees Fahr. (425 degrees Cent.) where austenite decomposition occurs in both steels, there is some sign of secondary hardening, particularly in the 10-hour curves of Fig. E. According to published hardness data, the secondary hardening which results from tempering in this high temperature range becomes much more pronounced as the hardening temperature is raised. Hence, the secondary hardening above 800 degrees Fahr. (425 degrees Cent.) is definitely associated with the presence of retained austenite. Tempering above 800 degrees Fahr. (425 degrees Cent.) conditions the austenite for transformation during the cooling to room temperature, and since the resulting product is martensite, there is a noticeable increase in hardness. On the other hand, after tempering above 1000 degrees Fahr. (540 degrees Cent.), the resulting hardness is relatively low despite extensive austenite transformation. This is because, as the tempering temperature is raised, there is progressively more and more isothermal transformation into a soft product and correspondingly less austenite available for transformation during cooling into hard martensite. In the same sense, the isothermal transformation of the austenite in the 1 per cent carbon-5 per cent chromium steel at temperatures of 500 to 600 degrees Fahr. (260 to 315 degrees Cent.) does not cause secondary hardening because the product is bainite rather than martensite.

Thus, the work by Zmeskal and Cohen, supplemented by these hardness and specific volume measurements, seem to offer a satisfactory explanation of the complex hardness changes which occur during the tempering of these high-carbon, high-chromium steels.

Written Discussion: By P. Payson and J. L. Klein, Eastern Research Laboratory, Crucible Steel Company of America, Harrison, N. J.

The authors have stated on page 386 that when these two chromium die steels are austenitized in the range 1700 to 1900 degrees Fahr. (925 to 1040 degrees Cent.), the retained austenite becomes less, the faster the cooling rate. Many years ago, Dr. Matthews published data which indicated that steels with about 1 per cent carbon and 2 to 4 per cent chromium had less retained austenite when they were water-quenched than when they were oil-quenched. We did not suspect that this relationship between cooling rate and amount of retained austenite could be extended to much slower cooling rates such as air



Figs. F to I—Structures of 1.5 Per Cent Carbon, 11.3 Per Cent Chromium, 0.5 Per Cent Molybdenum, 0.2 Per Cent Vanadium Steel. Austenitized at 2000 Degrees Fahr., Oil Quenched and Lime Cooled. Etched in 10 Per Cent Nital. $\times 1000$. Fig. F—Oil Quenched, Tempered 1050 Degrees Fahr. 30 Minutes. Etched 40 Seconds. Fig. G—Lime Cooled, Tempered 1050 Degrees Fahr. 30 Minutes. Etched 40 Seconds. Fig. H—Oil Quenched. Etched 15 Seconds. Fig. I—Lime Cooled. Etched 15 Seconds.

cooling, and cooling in lime. Indeed we should expect the opposite to be true. When these steels are cooled slowly, some of the carbides which have dissolved at the austenitizing temperature precipitate as the steel is cooling through the range between about 1600 and 1300 degrees Fahr. (870 and 705 degrees Cent.). This precipitation of carbides lowers the carbon content of the austenite, which

in turn raises the martensite point, and decreases the amount of austenite retained at room temperature.

Since by our technique we found less than 10 per cent austenite retained in similar steels when they were quenched in oil from temperatures below 1900 degrees Fahr. (1040 degrees Cent.),¹ we could not distinguish readily between the amounts of austenite retained in samples quenched in oil or cooled in lime from 1800 degrees Fahr. (980 degrees Cent.). However, we could easily distinguish between samples cooled at different rates from 2000 degrees Fahr. (1095 degrees Cent.). As was expected, we found that the oil-quenched samples had more retained austenite than the lime-cooled samples, and the amounts in the air-cooled samples were intermediate. The structures of the steels as cooled showed that the samples cooled in air and in lime had carbides precipitated at the austenite grain boundaries. Figs. F and G show by the quench temper technique the amounts of retained austenite in samples of a 1.5 per cent carbon, 11.3 per cent chromium, 0.53 per cent molybdenum, 0.24 per cent vanadium steel austenitized at 2000 degrees Fahr. (1095 degrees Cent.) and quenched in oil, and cooled in lime, respectively. Figs. H and I are the structures of samples of the same steel as cooled from 2000 degrees Fahr. (1095 degrees Cent.) by the two different rates. The hardness value of the samples as cooled are Rockwell C-55 for the oil quench; C-57.5 for the air cool; and C-59.5 for the lime cool, which corroborate the indications of the microstructures that the oil-quenched sample has more retained austenite than the lime-cooled.

The differences in the 1.0 per cent carbon, 4.6 per cent chromium, 1.0 per cent molybdenum, 0.25 per cent vanadium steel between the samples oil-quenched, air-cooled, and lime-cooled, from 2000 degrees Fahr. (1095 degrees Cent.), were not as great as in the higher chromium steel samples. However, the indications from the microstructures and hardness tests were similar, i.e., that the oil-quenched samples had more retained austenite than the air-cooled and lime-cooled samples.

Written Discussion: By G. M. Butler, research metallurgist, Allegheny Ludlum Steel Corp., Dunkirk, N. Y.

Figs. 1 and 2 of this informative paper disclose that more austenite is retained by slower cooling than by oil quenching. It may be of interest to note that this confirms observations made in the course of work published last year² on dimensional changes in these and similar steels. While attention was not specifically called to the effect of quenching versus slower cooling on retention of austenite, yet examination of the original data yields results in good agreement with that presented by Drs. Zmeskal and Cohen.

In my work, amount of retained austenite was estimated from magnetic saturation measurements. Fraction of austenite after quenching was obtained by subtracting the saturation value as quenched from that as annealed, and dividing by the annealed value. Samples were $\frac{1}{4}$ inch round x 2 inches long

¹P. Payson and J. L. Klein, "The Hardening of Tool Steels," *TRANSACTIONS, American Society for Metals*, Vol. 31, 1943, p. 218.

²G. M. Butler, Jr., "Study of Dimensional and Other Changes in Various Die Steels Due to Heat Treatment," *TRANSACTIONS, American Society for Metals*, Vol. 30, 1942, p. 191.

and were either oil-quenched or cooled at a rate approximating that of a $\frac{3}{4}$ -inch round bar cooled in still air.

Under these conditions, the following percentages of retained austenite were determined in the two types of steel studied in the present paper, cooled as shown from the indicated temperatures:

1 Per Cent Carbon—5 Per Cent Chromium—1 Per Cent Molybdenum Steel		
Hardening Temperature Degrees Fahr.	Oil-Quenched Per Cent	Slower Cool Per Cent
1675	8 Austenite	19 Austenite
1750	17 Austenite	23 Austenite
1825	36 Austenite	38 Austenite

1.5 Per Cent Carbon—12 Per Cent Chromium—0.75 Per Cent Molybdenum		
Hardening Temperature Degrees Fahr.	Oil-Quenched Per Cent	Slower Cool Per Cent
1750	10 Austenite	19 Austenite
1825	18 Austenite	23 Austenite
1900	34 Austenite	35 Austenite

If these figures are compared with the authors' values in Figs. 1 and 2, the agreement will be found to be very close. My 1.5 per cent carbon-12 per cent chromium samples showed even less retained austenite than those in the present paper, but my steels were very slightly lower in carbon, silicon, chromium, and molybdenum.

It seemed noteworthy to me that two independent investigations should show such similar results with different test methods.

Written Discussion: By W. E. Bancroft, chief metallurgist, Pratt & Whitney Division, Niles-Bement-Pond Co., West Hartford, Conn.

It is evident that the authors have reported a very painstaking and thorough study which adds greatly to the general knowledge of metallurgy. However, the ultimate value of such a piece of work lies in the practical application which can be made of its teachings in the routine heat treatment of parts made of the material studied.

Therefore, this discussion will attempt to present some of the comments and questions which come to mind when reviewing the report from the heat treater's standpoint.

It is interesting to note from the authors' tempering and retained austenite transformation curves the importance of time in the transformation of retained austenite during tempering. Figs. 6 and 9 indicate that tempering for the usual commercial period of 1 or 2 hours results in the transformation of a very small percentage of the retained austenite even within the "active" ranges of 400 to 600 degrees Fahr. (205 to 315 degrees Cent.) and above 900 degrees Fahr. (480 degrees Cent.). This fact would seem to amply justify the preference of some operators for very extended tempering times when heat treating parts made of these two steels. Undoubtedly, bringing the transformation of the retained austenite as near to completion as possible during tempering would result in improved physical properties and especially in increased stability in fragile die sections. However, here the question of hardness might come up. The authors have made no mention of hardness in their paper, possibly not

considering it to be within the scope of this particular study; but, if hardness values were shown and correlated with different degrees of transformation at the various temperatures and times, it would be of some assistance in making practical application of the information presented in this paper.

I wonder if the authors might have made any measurement of transformation of retained austenite during extended holding periods at room temperatures after quenching from various temperatures and before tempering. It is the writer's impression, from rough observation in the past, that the 1.5 per cent carbon-12 per cent chromium steel, at least, may start to transform some of its retained austenite at room temperature before tempering. It would be interesting to learn whether the authors' methods of investigation would reveal such a tendency and if so how fast it might proceed and what effect it would have on the further transformation during tempering.

Written Discussion: By W. H. Wills, metallurgist, Allegheny Ludlum Steel Corp., Dunkirk, N. Y.

The information brought out in this paper is a valuable addition to the literature on high-carbon, high-chromium steels. After study of this and a review of previous experimental work on these grades, the following comment is submitted regarding their commercial heat treatment:

The hardening range is generally understood to be rather wide and as stated in the paper, 1700 to 1900 degrees Fahr. (925 to 1040 degrees Cent.). The temperature used will be somewhat governed by the size of the tools. However, the fact that the amount of retained austenite and its stability are much increased as the hardening temperature is increased are good reasons for avoiding the upper end of the range. The holding time at temperature should be sufficient to insure proper solution of carbides for good wearing quality, but not so long as to produce an excess of retained austenite. The less the retained austenite the better the resistance to shock and the less the internal stresses set up in the structural changes that accompany the tempering operation.

The tempering of tools of these grades is largely carried out in two ranges, namely, 350 to 500 degrees Fahr. (175 to 260 degrees Cent.) when little or no shock is involved, and 900 to 1000 degrees Fahr. (480 to 540 degrees Cent.) when more toughness is required.

When the lower range is used the tools go into service having a structure with more or less retained austenite and the curves would indicate that the retained austenite would never be more than 30 to 50 per cent transformed. It would be interesting to compare the hardness, impact value, dimensional changes, and wearing quality of these steels with different degrees of austenite transformation.

When tempering in the higher range 900 to 1000 degrees Fahr. (480 to 540 degrees Cent.) rate of heating should not be too rapid in view of the sluggishness of retained austenite in the range 700 to 800 degrees Fahr. (370 to 425 degrees Cent.). According to the curves, the commonly used time of tempering, namely 2 to 4 hours, is hardly sufficient for 100 per cent transformation of the austenite. Rapid cooling from the tempering range should be avoided.

As a concluding remark, the various points brought out in this paper serve

to emphasize the precaution: "Do not rush the tempering of these grades," especially when dealing with large sizes.

Written Discussion: By Norbert K. Koebel, research director, Lindberg Engineering Co., Chicago.

The authors are to be congratulated on their splendid investigation on the kinetics of tempering the high-carbon, high-chromium tool steels. This information is of particular interest to the writer as it confirms his investigation on the difficulties encountered in practice in the hardening of the 1 per cent carbon-5 per cent chromium-1 per cent molybdenum air hardening tool steel. The writer would like to link his experience in the commercial hardening of these air hardening tool steels with the valuable information the authors have presented in their paper.

One of the variables the authors did not investigate is the effect of the carbon content on the amount of retained austenite formed during hardening and the effect of the tempering treatment on the retained austenite formed by higher or lower carbon contents. Off hand, one would not consider the carbon contents of each of the two steels under discussion as a variable, because the carbon content for each steel is held fairly constant in the melting and manufacturing process. In the commercial hardening of these steels, the carbon does not, however, always remain constant, especially at the surface. Inasmuch as the air hardening steels are chiefly used for tools and dies that are of such a shape or design which will not permit grinding after hardening, the effect of the carbon content on the surface, the most vital part of the tool, is of great importance.

The writer has found that the 1 per cent carbon-5 per cent chromium-1 per cent molybdenum air hardening type is a very peculiar steel and one that is very difficult to harden free from a soft skin. Increasing the amount of carbon in the steel, as is done by carburizing the surface, so greatly influences the steel to retain its austenite that only a very small percentage of hard constituents are formed after the air quench. To obtain the maximum hardness, this steel must be heat treated in a packing material or in a protective atmosphere or in a salt bath that is in direct equilibrium with the steel.

The table below shows the results obtained by heat treating the 1 per cent carbon-5 per cent chromium type of air hardening steel in three types of atmospheres: first, an atmosphere in equilibrium with the steel; second, one decarburizing to the steel; and third, one carburizing to the steel. The action of these atmospheres was checked by microscopic examination of the steels treated in each and by the change in weight method for evaluating a controlled atmosphere. These results show that a carburizing atmosphere can produce even a lower hardness, both to the Rockwell and to the file, than a decarburizing atmosphere. The degree of softness depends upon the degree of carburization or the degree of decarburization whichever may be the case.

Effects of Various Atmospheres on a 1.0 Per Cent Carbon-5.0 Per Cent Chromium-1.0 Per Cent Molybdenum Air Hardening Steel at 1750 Degrees Fahr.

Type Atmosphere	Change in Weight	Rockwell Hardness
Neutral	-0.00005 GM/CM ²	64 C
Decarburizing	-0.00172 GM/CM ²	58 C
Carburizing	+0.00372 GM/CM ²	50 C

The writer has found that if a large percentage of retained austenite is formed due to a carburized surface it is practically impossible to break it down to the hard constituents of martensite and carbides by a tempering treatment to get a hardness over 60 C. A draw temperature of 350 to 450 degrees Fahr. (175 to 230 degrees Cent.) normally used to obtain a hardness of 60 to 62 C will not break down the retained austenite because of its sluggish reaction at a low temperature. Temperatures in excess of 450 degrees Fahr. (230 degrees Cent.) may break down the austenite but at the same time will temper the martensite, thus making it impossible to obtain a hardness of 61 to 62 C required of blanking punches and dies.

On the other hand, increasing the carbon content of the 1.5 per cent carbon-12 per cent chromium type of air hardening tool steel does not materially increase the retained austenite so as to lower the Rockwell or file hardness of the steel to any appreciable extent. In fact this type of air hardening steel has always been very successfully hardened by packing in a carbonaceous material or by an atmosphere definitely carburizing, such as cracked liquid hydrocarbons, in order to prevent decarburization from occurring. Incidentally, the 1.5 per cent carbon-12 per cent chromium air hardening type and also the 2.5 per cent carbon-12 per cent chromium oil hardening type will pick up three times as much carbon at the same hardening temperature and in an atmosphere of the same carbon pressure as will the 1 per cent carbon-5 per cent chromium-1 per cent molybdenum air hardening type. In other words an atmosphere that is in direct equilibrium with the 1.5 or 2.5 per cent carbon-12 per cent chromium steels will be decarburizing to the 1 per cent carbon-5 per cent chromium type.

In the commercial hardening of the 1 per cent carbon-5 per cent chromium type, hardening temperatures in excess of 1750 degrees Fahr. (955 degrees Cent.) should be avoided or a low hardness will be obtained, due to a high percentage of retained austenite. This is pointed out and shown very clearly in the authors' paper. The writer has found that prolonged soaking at the hardening temperature should also be avoided because of the same reason. The best procedure for this type of steel seems to be to heat it directly up to 1725 degrees Fahr. (940 degrees Cent.) and air quench it after about 5 to 10 minutes' soak. On the other hand, the 1.5 per cent carbon-12 per cent chromium type is preheated at 1500 to 1600 degrees Fahr. (815 to 870 degrees Cent.) with a long soak and heated to 1850 degrees Fahr. (1010 degrees Cent.) for hardening with a soak. The soak at the preheat and high heat on this type of steel is necessary to obtain the maximum wear resistance that this steel is capable of giving.

In summarizing, an increase in carbon content, which may happen by surface carburization in heat treatment, increases the amount of retained austenite in the 1 per cent carbon-5 per cent chromium type of tool steel to such a great extent that both the Rockwell and file hardness are lowered. The high percentage of retained austenite formed by a carburized surface is so sluggish in response to breaking down that a 350 to 400-degree Fahr. (175 to 205-degree Cent.) draw does not materially increase the hardness of the steel. If temperatures in excess of 400 degrees Fahr. (205 degrees Cent.) are used, the martensite becomes tempered and a Rockwell hardness of 60 to 62 C required of

blanking punches and dies cannot be obtained. An increase in the carbon content by surface carburization of the 1.5 per cent carbon-12 per cent chromium type does not seem to materially affect the hardness of the steel, and, therefore, does not seem to increase the retained austenite.

Further investigation on the effects of the degree of carburization, or carbon content, on the degree of retained austenite formed on hardening, together with the effects of the tempering treatment on the retained austenite, would be of great interest.

Authors' Reply

The data presented by Mr. Antia and Mr. Howard, and obtained on the very same steels used by the authors, form a valuable supplement to this paper. There appears to be a basic similarity between the form of the primary S-curves and that of the retained austenite transformation curves, but as Mr. Antia points out, the details are not at all identical. Consequently, one should not rely on the behavior of primary austenite during hot quenching for predicting the behavior of retained austenite during tempering.

It is evident from Mr. Howard's discussion that the well-known retarded softening of these high-chromium steels on tempering up to 700 or 800 degrees Fahr. (370 or 425 degrees Cent.) is not attributable to the retained austenite decomposition, but is more likely related to the nature of the martensitic decomposition product. On the other hand, the secondary hardening that sets in on tempering above 800 degrees Fahr. (425 degrees Cent.) and that becomes more pronounced when high hardening temperatures are used is definitely caused by the decomposition of the retained austenite. The resulting product is hard martensite which forms on cooling from the tempering temperature.

Relative to the remarks of Messrs. Klein and Payson, our findings indicate that high-chromium tool steels, like many other alloy steels, retain less austenite on hardening if rapid quenching rates are employed. Apparently, the greatest amount of austenite is retained in a given steel if the cooling is fast enough to avoid the formation of pearlite or bainite but not so fast as to introduce stresses which stimulate the austenite-martensite transformation below the M-point. In high-carbon 5 per cent nickel steels, for example, the retained austenite content increases as the cooling medium is changed from water to oil to air, while still slower cooling rates achieved in lime or in the furnace result in decreasing amounts of retained austenite.³ In the case of the high-carbon high-chromium steels, the retained austenite content increases as the cooling medium is changed from water to oil to air to lime, while still slower cooling rates achieved in the furnace result in decreasing amounts of retained austenite. However, as shown by our Figs. 1 and 2, this relationship does not hold when the hardening temperature is excessively high, and then we are inclined to agree with Messrs. Klein and Payson that the precipitation of proeutectoid carbide takes place on slow cooling, and lowers the carbon content of the austenite sufficiently to promote its decomposition into martensite. In the lower carbon steels, the opposite effect may occur due to the formation of proeutectoid ferrite and the resulting build-up of carbon in the austenite.³

³F. S. Gardner, M. Cohen and D. P. Antia, "Quantitative Determination of Retained Austenite by X-rays," presented at the Annual Meeting of the American Institute of Mining and Metallurgical Engineers in New York, February, 1943.

The retained austenite determinations submitted by Dr. Butler are in reasonably good agreement with the values shown in Figs. 1 and 2 of the paper, particularly when it is considered that there were differences in the compositions, cooling rates and magnetic methods used in the two investigations. We are pleased to note that Dr. Butler has confirmed (1) that the 1 per cent carbon-5 per cent chromium steel retains more austenite than the 1.5 per cent carbon-12 per cent chromium steel when quenched from the same temperature in the range of 1700 to 2000 degrees Fahr. (925 to 1095 degrees Cent.), (2) that the amount of retained austenite in both steels increases rapidly with the hardening temperature, and (3) that more austenite is retained on air cooling than on oil cooling.

The hardness values requested by Mr. Bancroft are given in Mr. Howard's discussion. As Mr. Bancroft suggests, these high-chromium steels require quite long tempering treatments even within the "active" ranges to convert all of the retained austenite, especially if the hardening temperature is above 1800 degrees Fahr. (980 degrees Cent.). This is also brought out in Mr. Wills' discussion. From the standpoint of dimensional stability combined with maximum potential hardness, complete removal of the retained austenite is undoubtedly desirable. However, we have no information regarding the effects of residual austenite on the strength and toughness of these steels, and we are glad to have the opinions of both Mr. Bancroft and Mr. Wills that complete decomposition of the retained austenite should lead to improved mechanical properties. In this connection, multiple tempering may prove helpful in relieving stresses due to retained austenite transformation on cooling from the tempering temperature.

In reply to Mr. Bancroft's last question, the retained austenite in the 1 per cent carbon-5 per cent chromium steel undergoes noticeable decomposition at room temperature.⁴ This room temperature instability is most pronounced after hardening at about 1800 degrees Fahr. (980 degrees Cent.). Austenitizing above 1800 degrees Fahr. (980 degrees Cent.) causes increased stability due to the additional carbide solution, while austenitizing below 1800 degrees Fahr. (980 degrees Cent.) yields too little retained austenite to give much room temperature decomposition. After oil hardening from 1800 degrees Fahr. (980 degrees Cent.), we have found that about 3 per cent of austenite decomposes within 24 hours at room temperature. The rate of cooling from the hardening temperature also has an effect on the subsequent room temperature transformation, slower cooling rates being conducive to more transformation at room temperature. For example, about 6 per cent of austenite decomposes within 24 hours at room temperature after air cooling from 1800 degrees Fahr. (980 degrees Cent.), and about 7.5 per cent decomposes after lime cooling from 1800 degrees Fahr. (980 degrees Cent.). We have observed very little change beyond 24 hours. It also appears that these room temperature effects are more pronounced in the 1 per cent carbon-5 per cent chromium steel than in the 1.5 per cent carbon-12 per cent chromium steel.

The room temperature aging seems to exert little influence on the progress of austenite decomposition during tempering. Our experiments show that specimens air-cooled from 1800 degrees Fahr. (980 degrees Cent.) and aged at

⁴L. H. Penn, Bachelor's Thesis, Massachusetts Institute of Technology, April, 1942.

room temperature for 70 hours undergo initial austenite decomposition during tempering slightly earlier than do unaged specimens, but this difference disappears as the austenite transformation approaches completion.

Mr. Koebel's observations on the effect of carburization and decarburization are very timely. Judging from the rapid increase in the austenite stability due to increased carbide solution on austenitizing, one would expect that carbon penetration from a carburizing atmosphere would have a similar influence on the retained austenite near the surface of the steel. This is exactly what Mr. Koebel has found. We have also noted a soft skin on these steels after hardening in a carbonaceous atmosphere. The excessive retained austenite produced by carburizing or by too high a hardening temperature creates an important practical problem because the tempering temperatures required to decompose the austenite are so high that the coexisting martensite is overtempered, and the steel becomes unduly soft. Investigations are now under way at Massachusetts Institute of Technology to develop heat treatment cycles for converting the retained austenite without too much softening of the martensite.

THE METALLOGRAPHY OF COMMERCIAL MAGNESIUM ALLOYS

BY J. B. HESS AND P. F. GEORGE

Abstract

This paper summarizes the metallography of the commercial magnesium alloys. It describes a method of specimen preparation, suitable etchants, and the identification of the various microconstituents. Typical photomicrographs are shown, and the origin and meaning of the structures are discussed.

THE microstructures of magnesium alloys have been discussed at various times (1-6),¹ but these descriptions have not, in general, provided the concise metallographic techniques desirable for the routine examinations of commercial production. Therefore, it is the purpose of this discussion to describe the methods of specimen preparation and etching, to interpret the microstructures, and to provide typical photomicrographs obtained by these methods. The discussion is confined to the commercial magnesium alloys.

PREPARATION OF SPECIMENS

The methods of polishing magnesium alloys are governed by consideration for the basic softness of the matrix metal and the relatively greater hardness of most of the microconstituents, which are accordingly susceptible to objectionable relief polishing. In addition, during the coarse grinding stages the scratches from the preceding steps are removed so easily that care must be taken to prolong each grinding step sufficiently so that the surface layer of distorted metal is removed as well. Otherwise, upon subsequent etching the microstructure may exhibit false, confusing structures, such as twinning bands that appear to continue across grain boundaries without altering their directions (3), (7).

¹The figures appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. The authors are associated with the Metallurgical Department of The Dow Chemical Company, Midland, Michigan. Manuscript received June 22, 1942.

The actual polishing operations can be varied, as with other metals, depending upon the equipment available and upon the personal preference of the metallographer. A procedure that has proved satisfactory for the routine metallographic preparation of magnesium alloys is described in the Appendix.

Etching for Macro-Examination—Macro-etching can be accomplished by immersing the specimen in 10 per cent acetic acid or 10 per cent tartaric acid in water. The time of etching varies from 10 seconds to 2 minutes, depending upon the depth of etch required and the degree of polish of the surface prior to etching. This polish need not be so fine as that required for microscopic examination, and the chemical polishing method* is particularly applicable. After etching, the surface should generally be swabbed clean of the adhering reaction product and should be dried quickly to prevent staining. However, in some cases, especially when trying to show the flow lines in forgings, it is advantageous not to remove the reaction product. Thus, Fig. 1 shows a macrograph of a section of a cast magnesium bar where the reaction product has been removed, while Fig. 2 shows the flow lines in a magnesium alloy forging where the contrast has been greatly improved by etching somewhat more lightly and allowing the reaction product to remain on the surface.

The deep etching of ingot or billet slices provides only limited information. In general, porosity, shrinkage cracks, presence of entrapped oxide skins, and approximate grain size can be determined. Segregation is *not* indicated except under very special circumstances, though aluminum segregation is shown to some extent if the sample has first been fully aged. Manganese segregation can best be determined by radiographing the billet slice. The deep etching is accomplished by total immersion in 10 to 25 per cent acetic acid for 2 to 3 minutes. A fine tool cut or smooth grinding operation usually provides adequate preliminary surface preparation.

Etching for Micro-Examination—The etchants used for micro-examination are determined primarily by the physical condition of the alloy. The time of etching, too, depends primarily upon the physical condition and may vary widely from 5 to 10 seconds for the "as-cast" or "aged" condition to 1 to 2 minutes for solution heat treated condition.

For sand cast, permanent mold, and die cast metal in the "as-cast" condition and for practically all the alloys in the aged conditions,

*See Appendix.

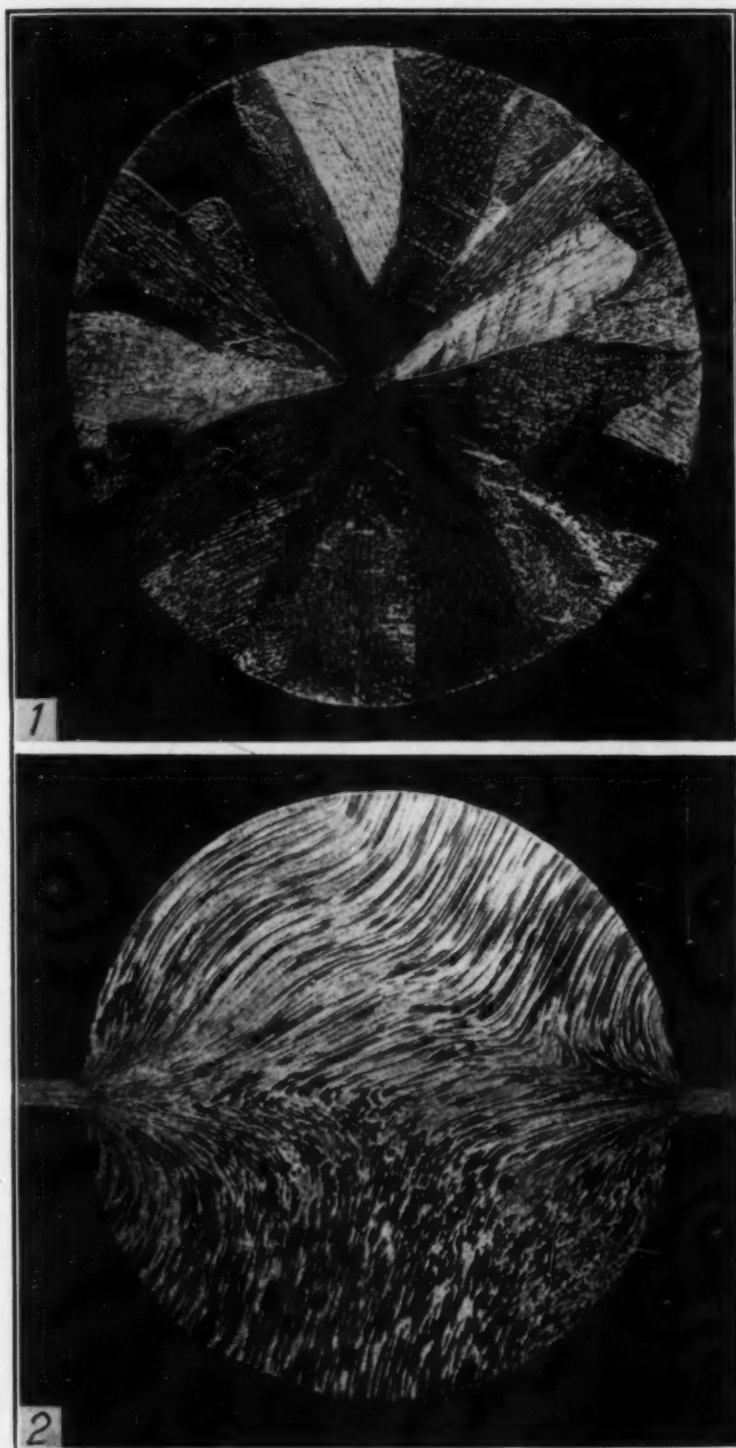


Fig. 1—Section of Cast Pure Magnesium Bar. Etched for 2 Minutes in 10 Per Cent Acetic Acid. $\times 3.5$.

Fig. 2—Flow Lines in Dowmetal J-1 (Mg-6.5 Al-0.7 Zn-0.2 Mn) Forging. Etched 15 Seconds in 10 Per Cent Tartaric Acid. $\times 5$.

the "glycol etchant" is perhaps the best. It has the following composition:

	Per Cent by Volume
Ethylene glycol	75
Conc. nitric acid	1
Distilled water	24

For metal in the solution heat treated condition, and for the wrought alloys in general, 10 per cent tartaric acid or "acetic-glycol" is satisfactory. "Acetic-glycol" is a modification of the "glycol etchant" and has the following composition:

	Per Cent by Volume
Ethylene glycol	60
Glacial acetic acid	20
Conc. nitric acid	1
Distilled water	19

The proportions are somewhat critical, so that accuracy in preparation is necessary for best results.

Another valuable etchant, "phospho-picral", is composed of:

Orthophosphoric acid	
(Sp. Gr. 1.70)	0.7 ml.
Picric acid	4.0 g.
Ethyl alcohol	100 ml.

It should be applied either by light swabbing or by immersion with gentle agitation. This etchant darkens all magnesium solid solution areas and leaves all other phases except Mg_2Sn unchanged. It is particularly useful for quickly estimating the amounts of undissolved compound in solution heat treated metal because of the extreme contrast between the darkened matrix and the uncolored compound. The dark reaction product which identifies the magnesium solid solution is rather loosely adherent until it has been dried, so that care should be exercised during swabbing and washing in order not to blur or obliterate the detail present in the microstructure.

IDENTIFICATION OF ALLOYING CONSTITUENTS

Nomenclature—Before proceeding to the identification of the various phases that occur in the microstructures, it is appropriate to outline the scheme of nomenclature which has been employed. It will be evident that the system is a modification and an extension of the scheme proposed by Fink and Willey (8). While the plan may seem unnecessarily complex and unwieldy, the authors feel that the exactness of phase identification that it provides in those cases where

simple composition is still unknown are adequate justification for its use. In brief it is as follows:

1. Each phase is designated by a successive letter of the Greek alphabet in order of increasing amount of the secondary element up to 50 atomic per cent. Phases are numbered in both directions from the terminal elements.

2. Following the Greek letter the symbols of the elements necessary to the formation of the phase are placed in parentheses and are separated by hyphens, the element of major amount being placed first. Where a definite chemical formula has been determined, such formula is substituted for the above inexact notation.

3. When it is desired to indicate the presence of some other element or elements as a solute in the phase, that condition is shown by placing the symbols of the solute elements after the parentheses and enclosing the entire designation in brackets.

As an example of the above conventions, the most common intermetallic phase in the commercial magnesium alloys would be designated $[\beta(\text{Mg-Al})\text{-Zn}]$. Here $\beta(\text{Mg-Al})$ indicates that the constituent is the second homogeneous phase in the magnesium-aluminum system in sequence from the magnesium terminal of the diagram, and that zinc is likewise present in solid solution but is not an element essential to the formation of the phase.

Aluminum—Of the various alloying elements, aluminum is the most important commercially because of its powerful effect in improving the physical properties. Although many researches have been conducted upon the entire binary system, considerable disagreement still exists concerning the reactions and phases in the central portion between $\beta(\text{Mg-Al})$ and $\beta(\text{Al-Mg})$. Fortunately, this region is unimportant in either the commercial alloys of magnesium or of aluminum.

At the magnesium end, according to the careful study of Hume-Rothery and Raynor (9), the system is eutectic as Fig. 3 shows, with the eutectic point falling at 819.0 degrees Fahr. (437.2 degrees Cent.) and 32.2 per cent aluminum. At the eutectic temperature the $\alpha(\text{Mg})$ lattice is able to dissolve 12.6 per cent aluminum; this solid solubility decreases to 2.6 per cent at 300 degrees Fahr. (150 degrees Cent.) (10).

Although the aluminum contents of all the commercial alloys are within the maximum solubility range, the slow diffusivity of aluminum in the $\alpha(\text{Mg})$ phase leads to pronounced solid solution

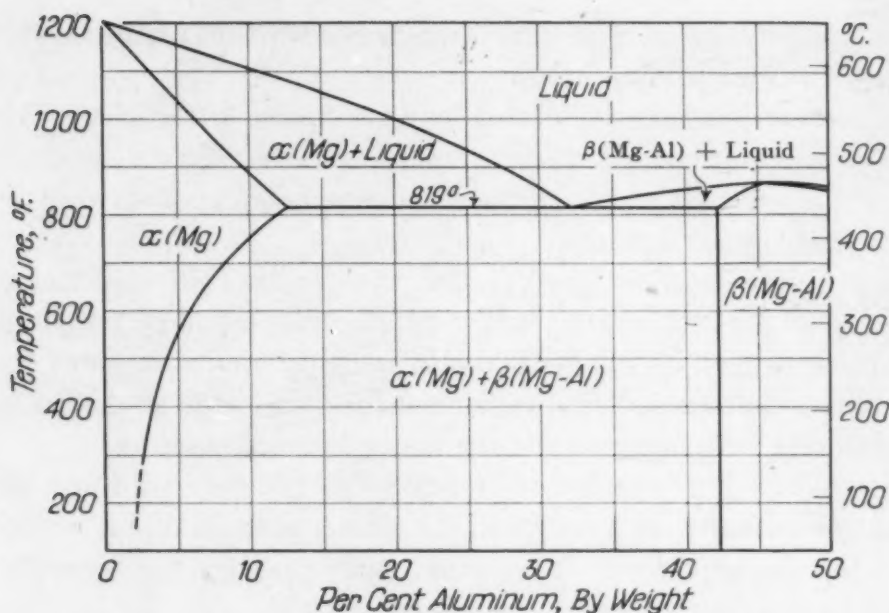


Fig. 3—Magnesium End of Magnesium-Aluminum Constitutional Diagram (9, 10).

coring and segregation during freezing. While it would ordinarily be expected from the nature of the constitutional diagram that such an alloy would have a microstructure consisting of cored, primary $\alpha(\text{Mg})$ dendrites and a eutectic composed of $\alpha(\text{Mg})$ and $\beta(\text{Mg-Al})$, such a eutectic structure has not yet been observed. Instead, the $\beta(\text{Mg-Al})$ phase occurs as clear white, massive, irregular crystals. These crystals have frequently been called the "primary compound", although it is still uncertain whether this phase freezes as a true primary crystal from the last portion of the melt that has become hypereutectic as a result of undercooling, or whether the phenomenon is due to very rapid coalescence and growth in the temperature range immediately under the freezing point of the crystals which initially froze eutectically.

Thus aluminum occurs in magnesium alloys both in solid solution as $[\alpha(\text{Mg})-\text{Al}]$ and as the intermetallic phase $\beta(\text{Mg-Al})$. In its massive "primary" form $\beta(\text{Mg-Al})$ is clear white and in slight relief from polishing. It is outlined, but otherwise unattacked, by the common etchants. When precipitated from solid solution, this compound forms a lamellar structure similar in appearance to the pearlite in steel, except at very low aging temperatures where it appears as fine, almost unresolvable particles having a globular shape. Fig. 4 shows the usual appearance of the massive "primary" $\beta(\text{Mg-Al})$ and

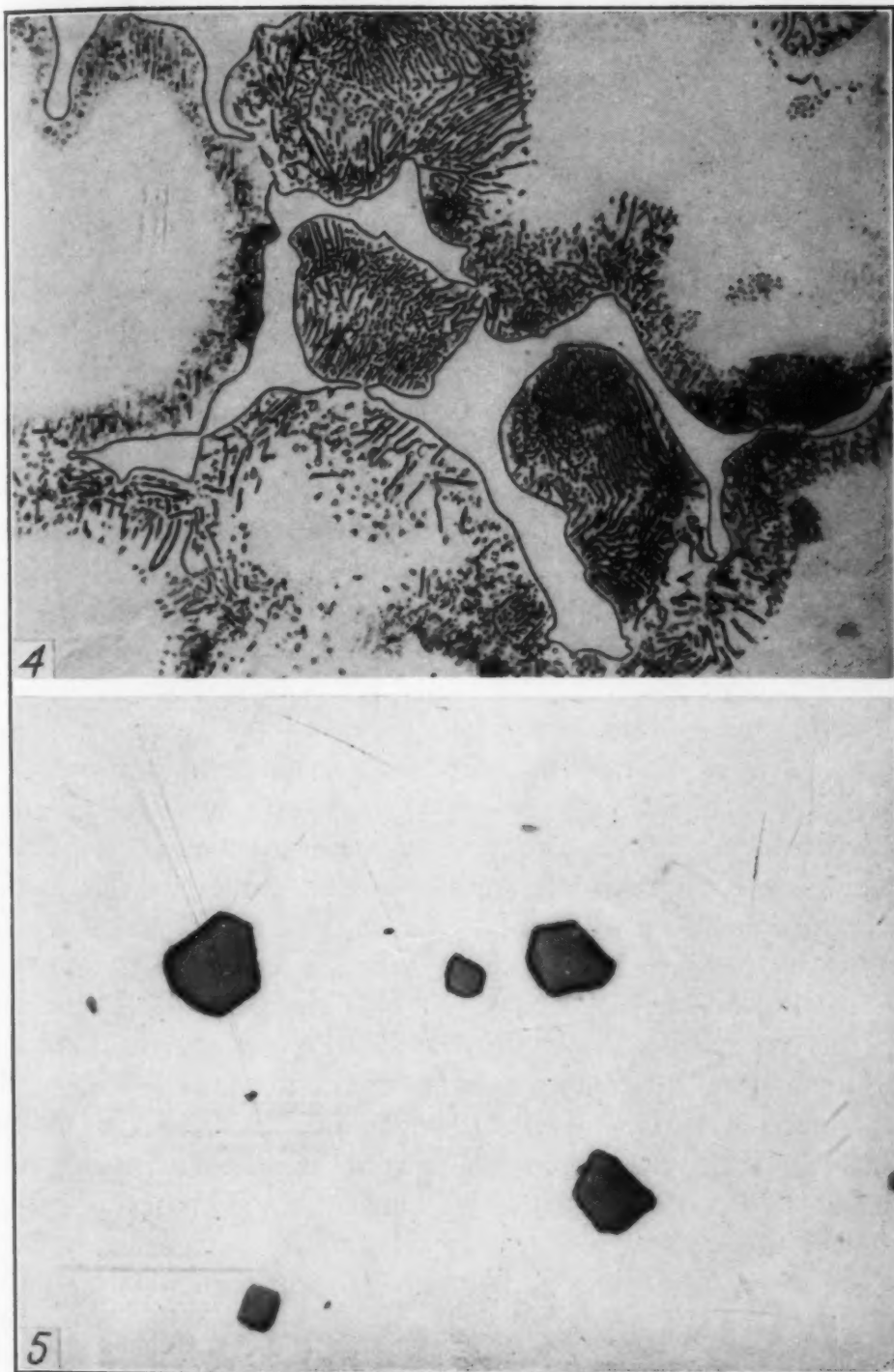


Fig. 4— β (Mg-Al) Constituent Showing Both the Massive "Primary" Particles and the Lamellar Precipitation. Etched 5 Seconds in Glycol Etchant. $\times 500$.

Fig. 5—Manganese Constituent. Unetched. $\times 500$.

also the lamellar formation in which it precipitates from super-saturated [α (Mg)-Al]. Occasionally the "primary" β (Mg-Al) exhibits a speckled appearance or even a ragged, filigreed appearance when the eutectic degeneration is incomplete.

Zinc—Zinc in binary magnesium-zinc alloys forms an inter-metallic compound which cannot be distinguished microscopically from β (Mg-Al). However, in the commercial alloys zinc is only added in conjunction with aluminum and in lesser amounts than the aluminum additions. In this condition zinc has practically no effect, except in the specific instances noted later, in altering the phase relationships in these alloys, so that from the metallographic standpoint all may be considered essentially as pure magnesium-aluminum alloys. The zinc appears only in solid solution as [α (Mg)-Al-Zn] and [β (Mg-Al)-Zn], and the microscopic appearance of the micro-constituents of the Mg-Al-Zn alloys is similar to that of Fig. 4. In this condition zinc improves the physical properties and counteracts the bad effects of heavy metal impurities on the resistance to salt water corrosion.

Manganese—Manganese is added to all the commercial magnesium alloys to improve the corrosion resistance to salt water. It appears microscopically as primary crystals with an angular contour and a bluish-gray color. The particles are in pronounced relief from polishing, and may characteristically exhibit circle-pits surrounding the particles which are caused by polishing. The particles are unaffected by etching, but the circle-pits are considerably enlarged. The solid solubility of manganese in pure magnesium decreases from 3.4 per cent at 1193 degrees Fahr. (645 degrees Cent.) to approximately nil at room temperature, but it has only a negligibly small effect in hardening and strengthening the alloys when heat treated (4). In the commercial magnesium-aluminum alloys the liquid solubility of manganese is considerably decreased from the solubility in pure magnesium so that less total manganese is found in these alloys, and most of it occurs as primary crystals. Fig. 5 shows the typical appearance of these primary manganese crystals.

Silicon—Silicon occurs in the commercial magnesium alloys as the intermetallic compound Mg_2Si . In normal small contents this Mg_2Si constituent has sometimes been mistaken for manganese, but it differs from manganese in having a more watery blue color and a more angular outline and in not having so much relief from polishing. Thus, Fig. 5a shows the typical appearance of the Mg_2Si con-

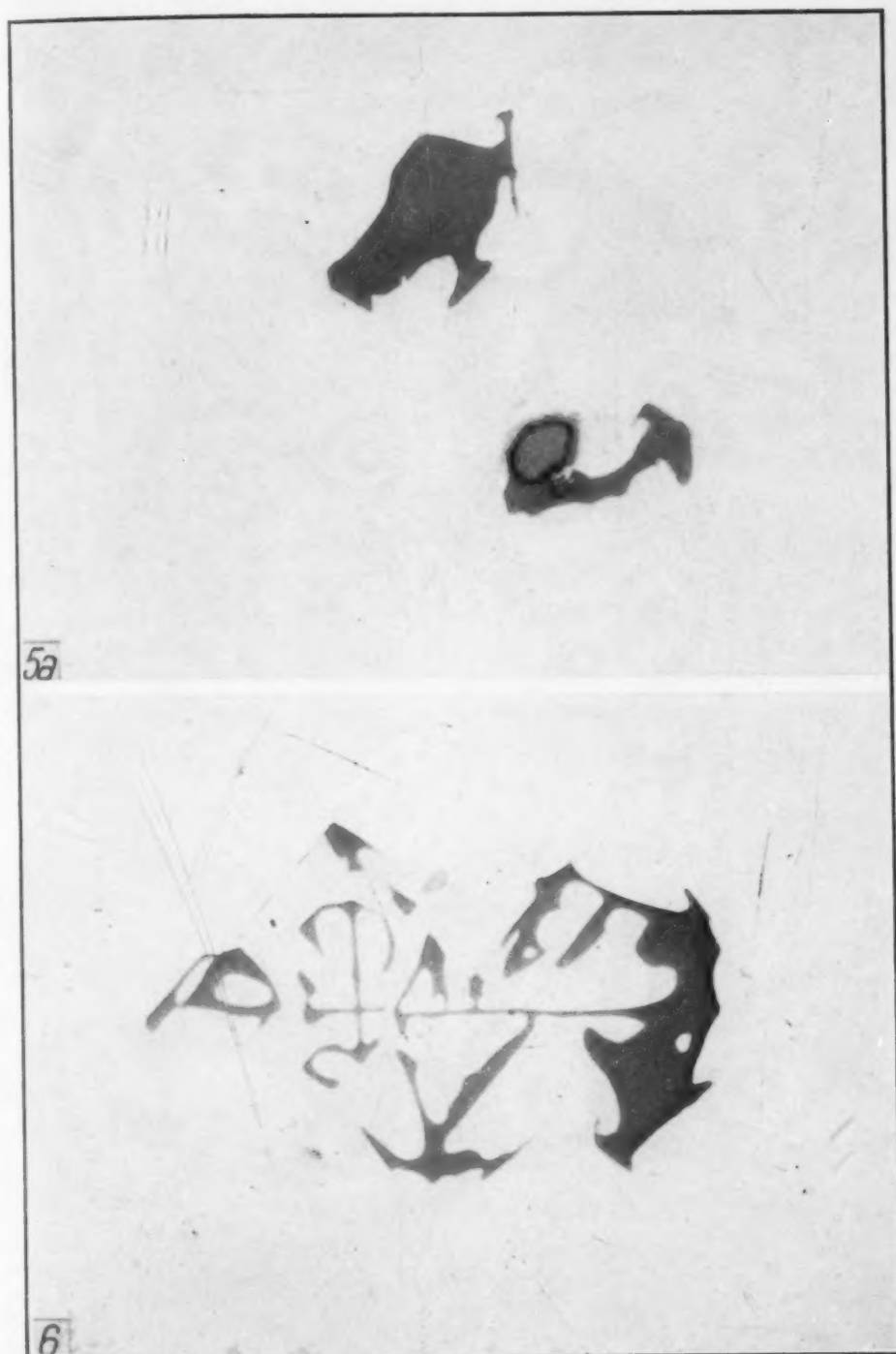


Fig. 5a—Typical Appearance of Mg_2Si Constituent, With an Included Manganese Particle. Unetched. $\times 1000$.

Fig. 6—"Chinese Script" Appearance of Mg_2Si Constituent. Unetched. $\times 500$.

stituent, one particle of which also contains an included manganese particle. When the silicon content is greater than about 0.2 per cent

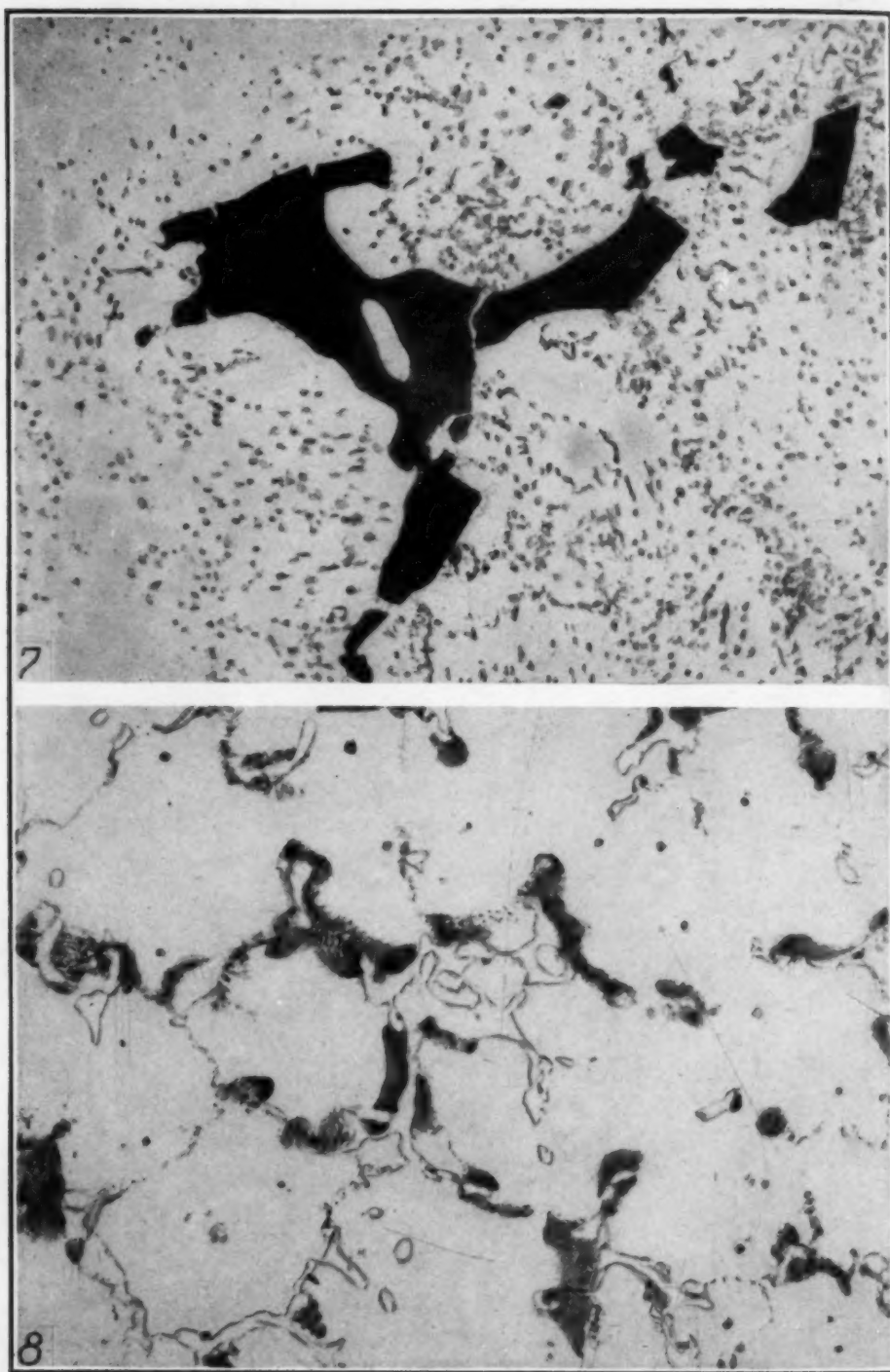


Fig. 7— Mg_2Sn Constituent. Etched 5 Seconds in Glycol Etchant. $\times 500$.

Fig. 8—Typical Sand Cast Structure of Dowmetal C (Mg-9 Al-2 Zn-0.1 Mn). Etched 5 Seconds in Glycol Etchant. $\times 250$.

in the aluminum-containing magnesium alloys, the phase develops the "Chinese script" appearance illustrated in Fig. 6. The common

etchants do not affect this phase except to outline it sharply, and perhaps to tarnish its color slightly. However, tartaric acid etchants roughen and pit it. The solid solubility of silicon in magnesium is very small, probably below 0.003 per cent at the eutectic temperature.

Cadmium—Since cadmium has a wide range of solid solubility in $\alpha(\text{Mg})$, this element is always found as $[\alpha(\text{Mg})\text{-Cd}]$ in those commercial alloys to which it is added, and, as such, it is not visible microscopically. In the “as-cast” condition this element produces pronounced solid solution coring which is easily demonstrated with the diluted nitric acid etchants.

Tin—Tin in commercial magnesium alloys appears both in the intermetallic compound Mg_2Sn and as a solute element dissolved in the $\alpha(\text{Mg})$ phase. Fig. 7 shows the typical appearance of the Mg_2Sn constituent. In the unetched condition this constituent is a dull grayish-blue, but in the etched condition it may be colored either tan to brown or a deep blue, depending upon the period of etching.

CAST ALLOYS

The magnesium alloys used for sand casting contain aluminum, or aluminum and zinc, along with minor amounts of manganese and silicon.

Fig. 8 shows a typical sand cast structure of a Mg-9Al-2Zn-0.1Mn alloy.* In this micrograph the clear white massive $\beta(\text{Mg-Al})$ can be seen in slight relief and sharply outlined from etching. These massive crystals are the result of some form of eutectic degeneration during freezing as previously explained. They behave, however, like an ordinary eutectic mixture in that they can be remelted at the eutectic temperature and can be quenched to exhibit a true eutectic appearance as Fig. 9 shows. This effect is important in the heat treatment of alloys containing this microstructure.

While Fig. 8 shows all of this massive compound lying in the grain boundaries as a semi-continuous network which is helpful in estimating grain size, this condition is not necessarily true in all cases. Whenever prominent branched dendrites have formed, the massive compound may also be found lying in the dendritic interstices where

*In this conventional method for indicating the nominal analyses, the coefficients of the chemical elements indicate the respective amounts of those elements in per cent by weight except in the case of Mg itself. Here the coefficient is not written but is understood to represent the remainder, less trace and impurity contents.

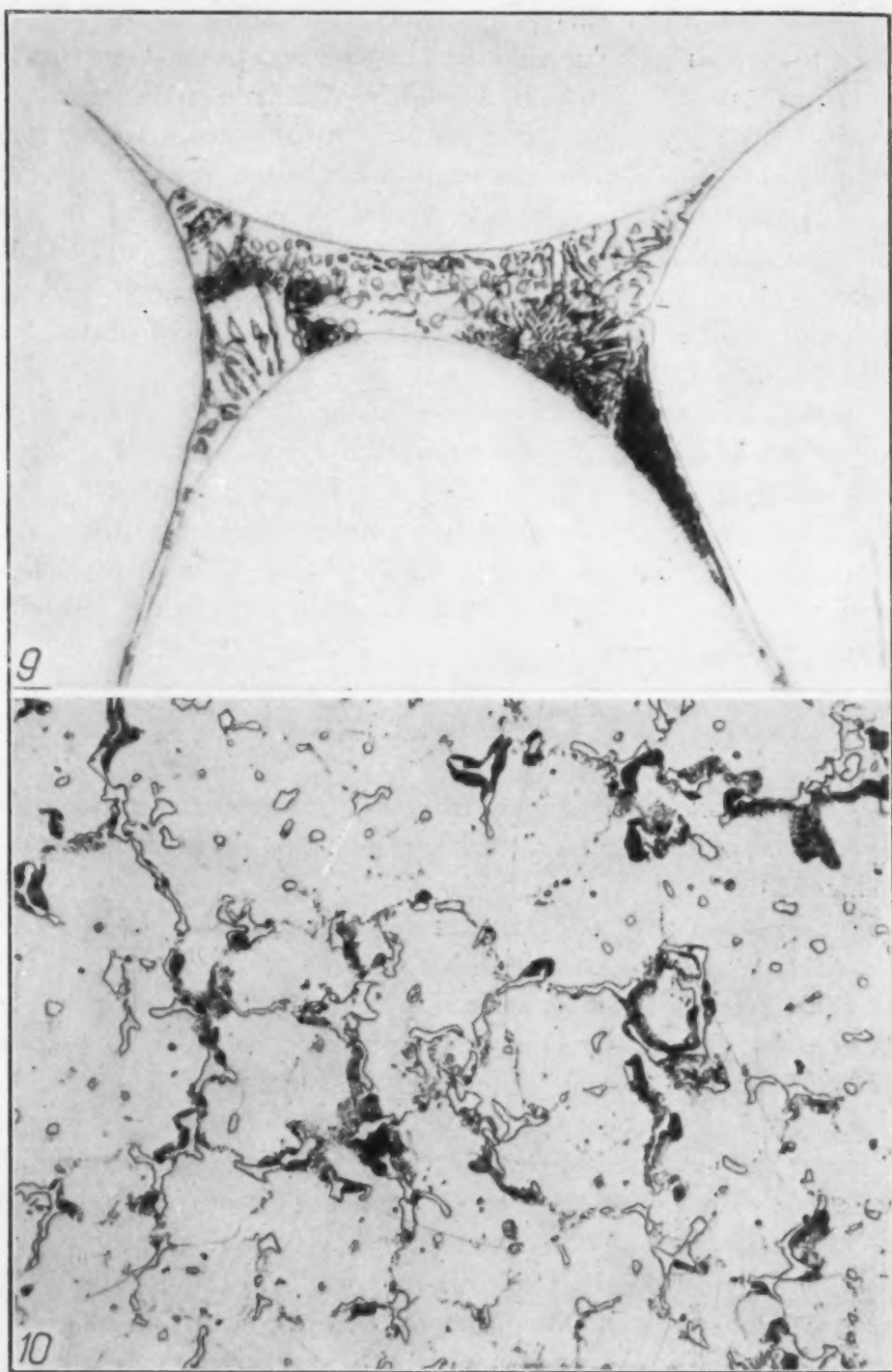


Fig. 9— α (Mg) + β (Mg-Al) Eutectic, Retained by a Drastic Quench from Above the Eutectic Temperature. Etched 5 Seconds in Glycol Etchant. $\times 1500$.
Fig. 10—Typical Structure of Dowmetal C (Mg-9 Al-2 Zn-0.1 Mn) Cast in Permanent Mold. Etched 5 Seconds in Glycol Etchant. $\times 250$.

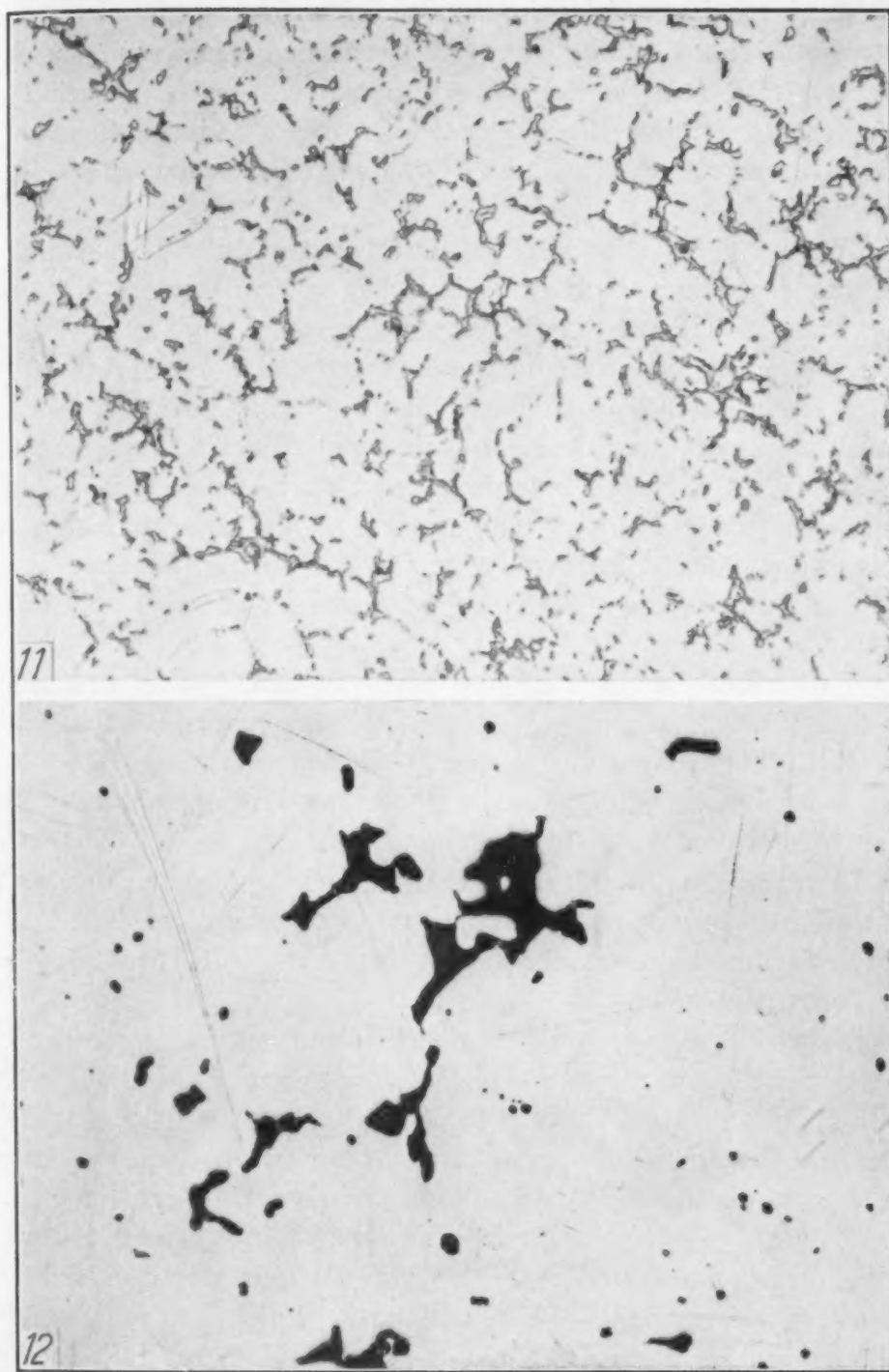


Fig. 11—Typical Die Cast Structure of Dowmetal R (Mg-9 Al-0.6 Zn-0.2 Mn). Etched 5 Seconds in Glycol Etchant. $\times 500$.

Fig. 12—Microporosity in a Magnesium Alloy Sand Casting. Unetched. $\times 100$.

they tend to give a false impression of a finer grain size than is actually the case. In any event, the accuracy of grain size measurement is increased if the samples are first given a partial solution heat treatment to remove the evidence of coring, and are then cooled rapidly in air so that a line of precipitation occurs at the grain boundaries.

In Fig. 8 the massive $\beta(\text{Mg-Al})$ compound is surrounded by the same phase in a lamellar, pearlite-like structure which is a result of precipitation from the $[\alpha(\text{Mg})-\text{Al}]$ phase during cooling in the mold. Due to the mechanism of freezing the $\alpha(\text{Mg})$ phase becomes richer in dissolved aluminum as its crystallization proceeds, so that the regions near the grain boundaries adjacent to the "eutectic" are richest in dissolved aluminum and may exceed the solubility limit permitted at a lower temperature. This supersaturation then leads to precipitation in these regions as the cooling proceeds.

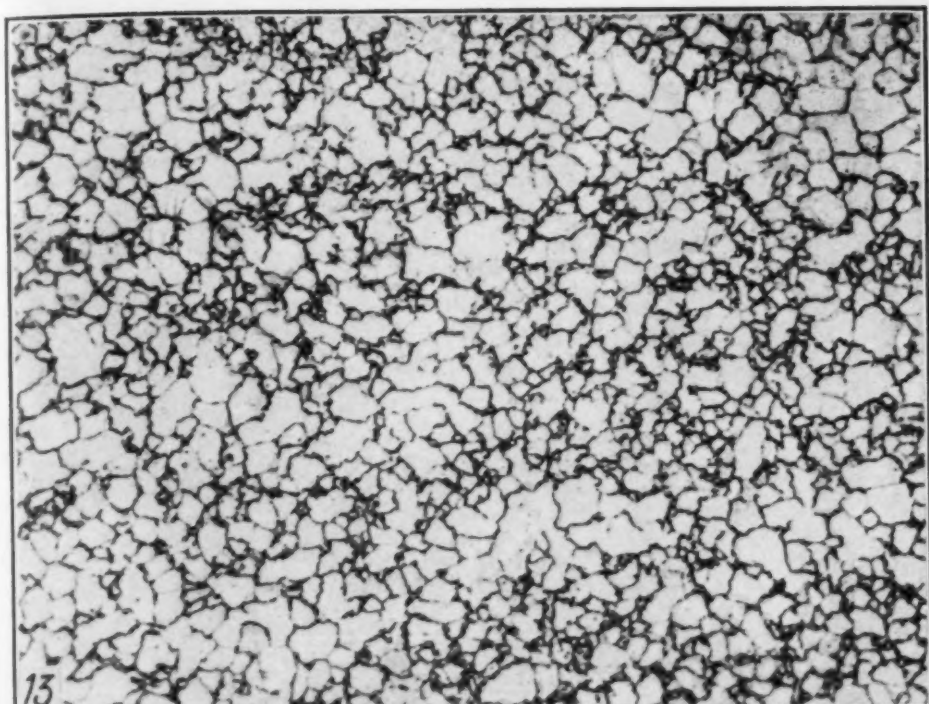
Several manganese crystals can also be seen in this photomicrograph.

The microstructures of the other common sand cast alloys, Mg-6Al-3Zn-0.2Mn and Mg-10Al-0.1Mn, are similar to that shown in Fig. 8. The amount of massive $\beta(\text{Mg-Al})$ varies slightly with the aluminum content, and the amount of lamellar precipitated $\beta(\text{Mg-Al})$ varies with the speed of cooling.

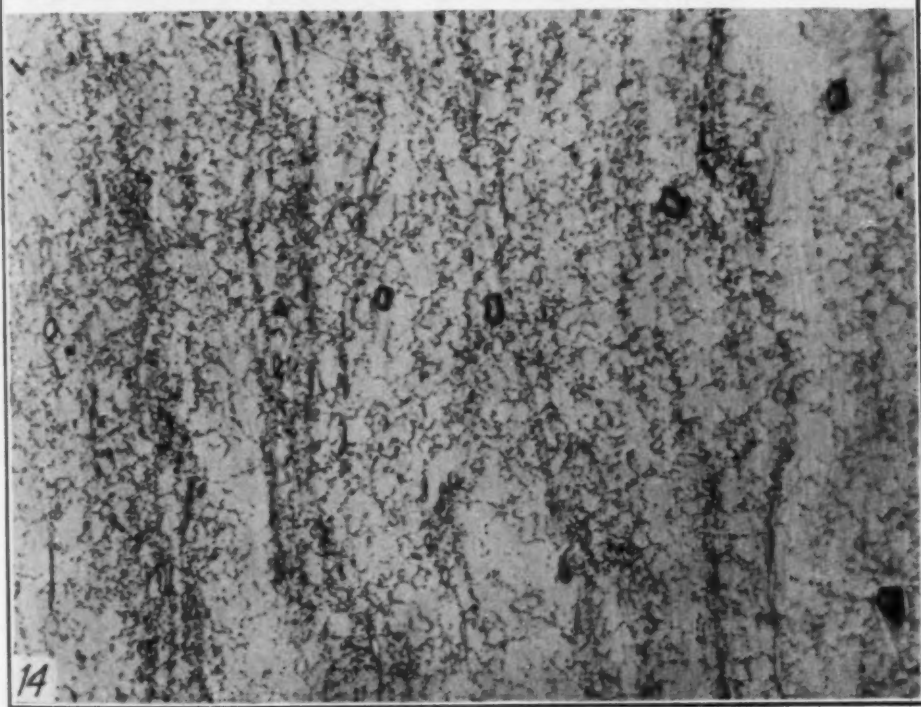
Permanent mold castings have much the same structure as the sand castings except that the grain size is somewhat smaller. Fig. 10 shows the microstructure of a Mg-9Al-2Zn-0.1Mn alloy cast in a permanent mold.

Die castings have a much finer structure than any other cast condition. Fig. 11 shows a typical die cast structure for a Mg-9Al-0.6Zn-0.2Mn alloy. The very rapid cooling of the die castings explains the absence of the precipitated $\beta(\text{Mg-Al})$ and the appearance of the pronounced solid solution coring of the $\alpha(\text{Mg})$ regions.

A defect that may occur in magnesium alloy castings is that of microporosity, illustrated in Fig. 12. This defect is caused by the lack of proper feeding: The last portion of the melt, i.e., the aluminum rich portion of approximately eutectic composition, has failed to feed into the shrinkage cavities around the primary $\alpha(\text{Mg})$ dendrites. This condition can be eliminated to a great extent by proper foundry practice and design of the molds.



13



14

Fig. 13—Longitudinal Section of Extruded Dowmetal O (Mg-8.5 Al-0.5 Zn-0.2 Mn). Etched 15 Seconds with Acetic-Glycol. $\times 250$.

Fig. 14—Longitudinal Section of Press Forging of Dowmetal O (Mg-8.5 Al-0.5 Zn-0.2 Mn). Etched 15 Seconds in Acetic-Glycol. $\times 250$.

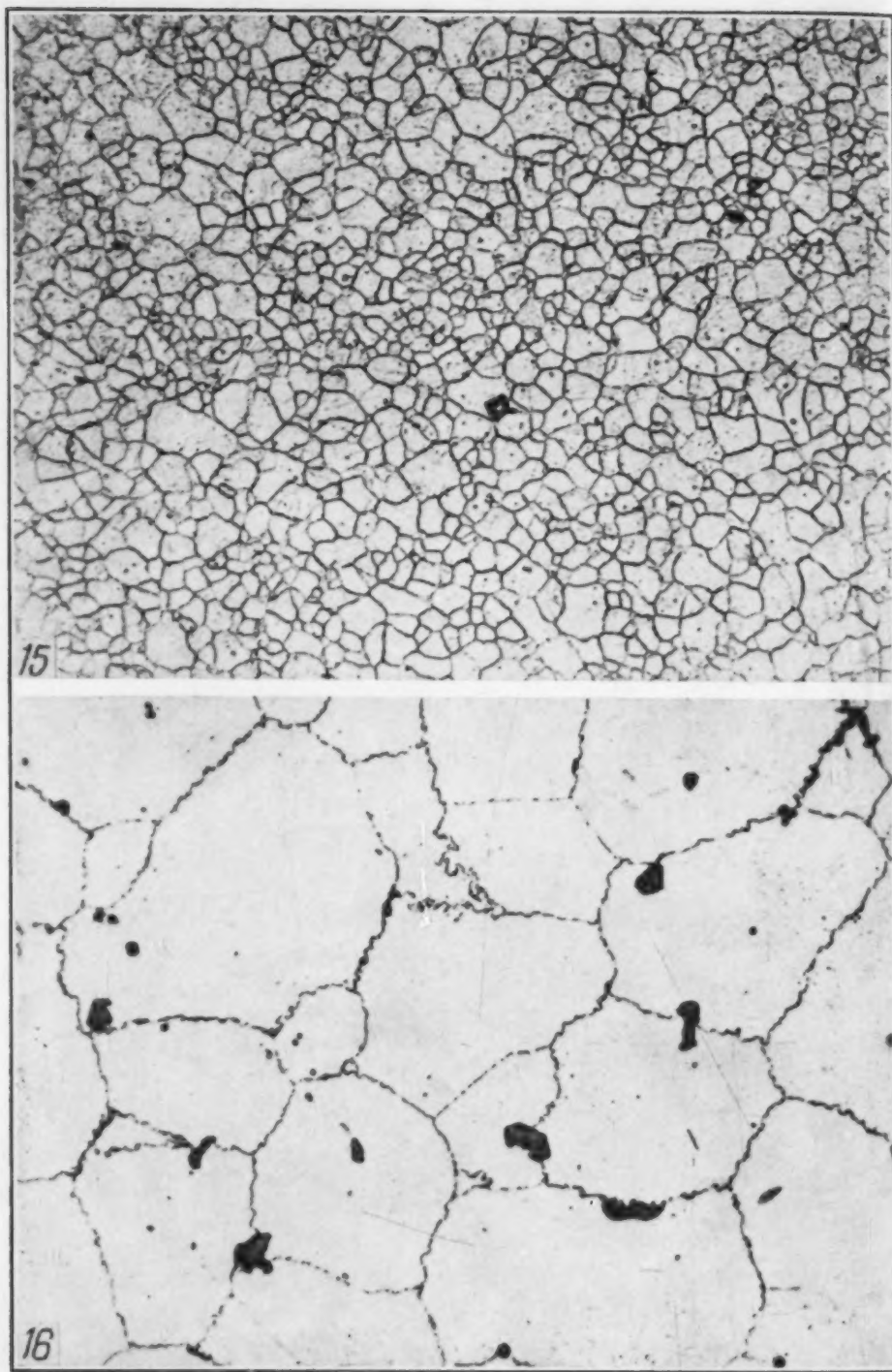


Fig. 15—Longitudinal Section of Rolled and Annealed Sheet of Dowmetal M (Mg-1.5 Mn). Etched 10 Seconds in Acetic-Glycol. $\times 250$.

Fig. 16—Solution Heat Treated Sand Cast Dowmetal C (Mg-9 Al-2 Zn-0.1 Mn). Etched 5 Seconds with Acetic-Glycol. $\times 250$.

WROUGHT ALLOYS

Extrusions—Many of the magnesium alloys are extruded. In this condition the grain structure of the cast billet has been broken down and recrystallized into fine-grained metal. Most of the $\beta(\text{Mg-Al})$ constituent had already been dissolved when the billet was heated prior to being extruded, and the final extruded structure consists of fine $[\alpha(\text{Mg})-\text{Al}]$ grains, with perhaps some $\beta(\text{Mg-Al})$ precipitation if the rate of cooling from the extrusion temperature has been slow enough to permit it to form. Fig. 13 shows a longitudinal section of an extruded Mg-8.5Al-0.5Zn-0.2Mn alloy.

Forgings—Forgings are either press or hammer forged from previously extruded stock. The microstructure is not essentially different from extruded metal. Fig. 14 shows the typical structure of a press forging from Mg-8.5Al-0.5Zn-0.2Mn alloy, while Fig. 2, mentioned previously, shows the flow lines that are typical of forged material.

Rolled Sheet—Cast billets of magnesium alloys are extruded into rolling slabs and then rolled into sheet. This rolled material is characterized especially by its fine grain size. Fig. 15 shows the structure of a typical rolled and annealed Mg-1.5Mn alloy.

EFFECT OF HEAT TREATMENT

Solution Heat Treatment—Solution heat treating magnesium alloy castings of the magnesium-aluminum or magnesium-aluminum-zinc types increases their tensile strength, ductility, and toughness. This treatment consists ideally of holding the cast alloy at an elevated temperature where the excess $\beta(\text{Mg-Al})$ constituent can be dissolved completely in the $\alpha(\text{Mg})$ phase, and then of cooling rapidly to maintain this condition at normal temperatures. Fig. 16 shows a typical microstructure after such a solution heat treatment. The small particles of Mn and Mg_2Si are not noticeably affected by the heat treatment.

In order to prevent a defect called "burning", the solution heat treatment is usually performed in two steps, which consists of an initial preheat with a gradually increasing temperature and a holding period at a specified maximum temperature. This "burning", illustrated in Fig. 17, is the result of the melting and oxidation of the eutectic constituent formed during solidification. Since the melting

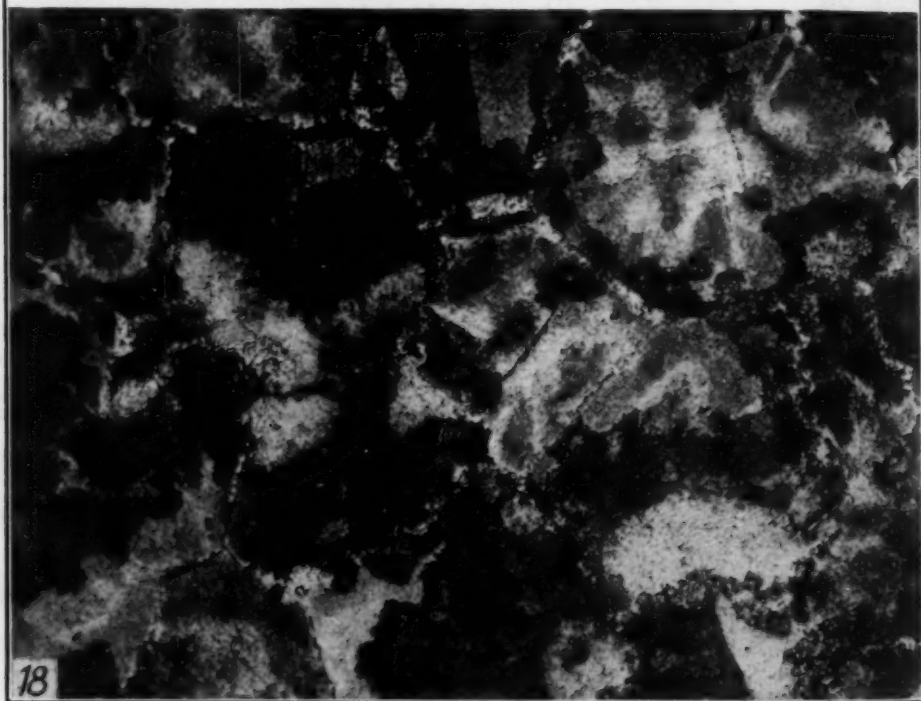
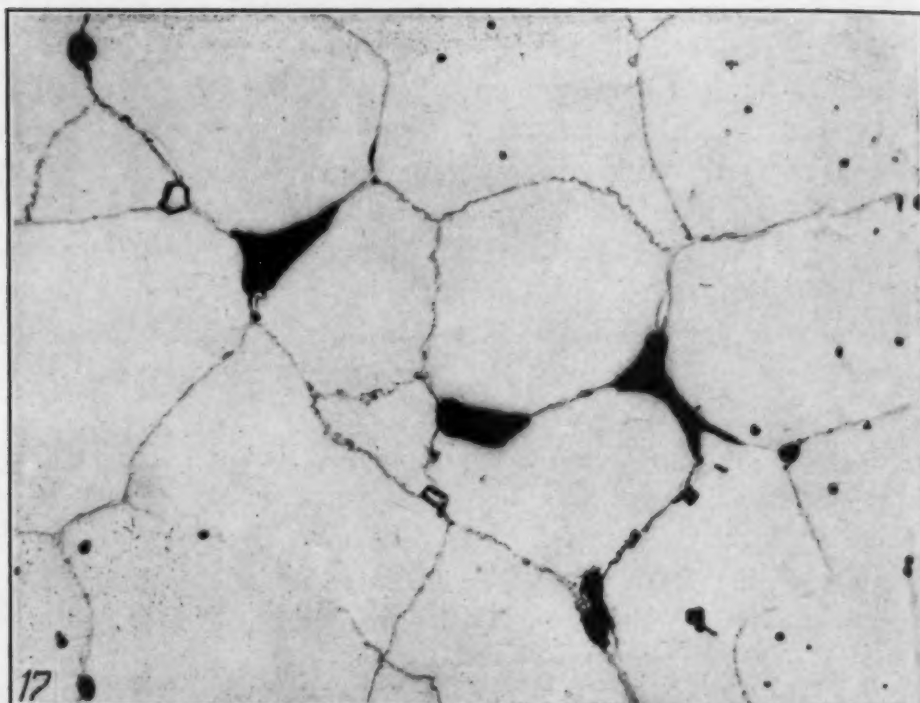


Fig. 17—"Burning" Caused by Improper Solution Heat Treatment of a Cast Magnesium Alloy. Etched 5 Seconds in Glycol Etchant. $\times 150$.
Fig. 18—Typical Aged Condition of Cast Dowmetal C (Mg-9 Al-2 Zn-0.1 Mn). Etched 5 Seconds in Glycol Etchant. $\times 250$.

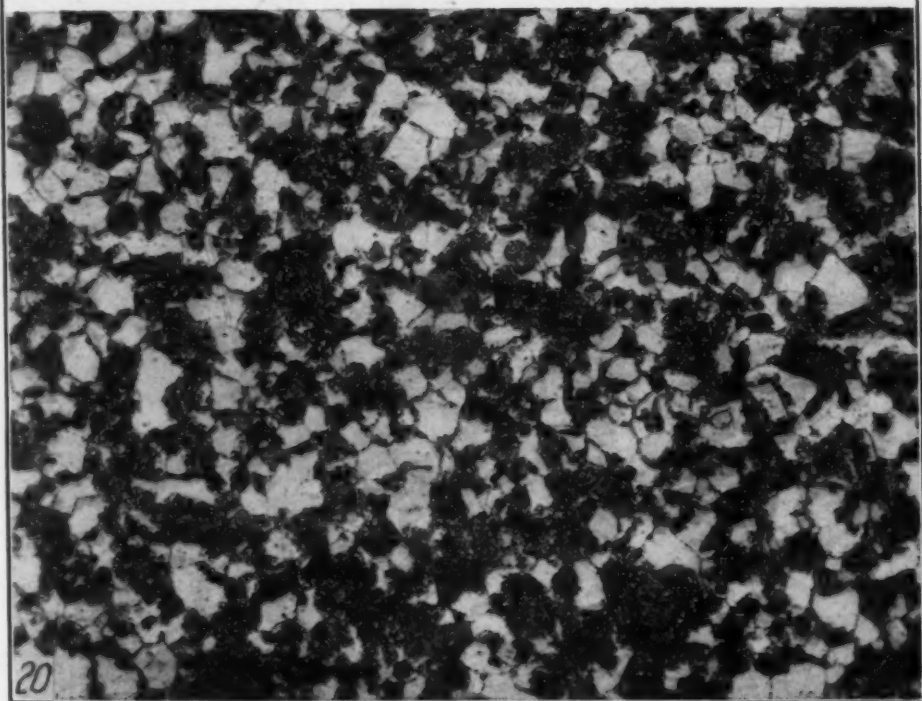
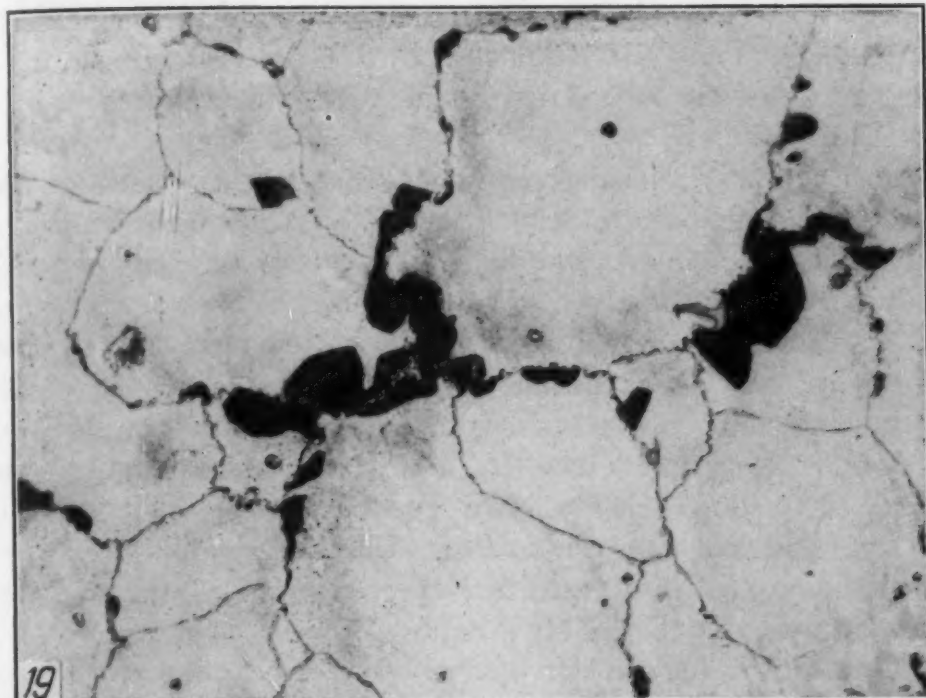


Fig. 19—Typical Aged Condition of Cast Dowmetal H (Mg-6 Al-3 Zn-0.2 Mn). Etched 5 Seconds in Glycol Etchant. $\times 250$.

Fig. 20—Typical Aged Condition of Extruded Dowmetal O (Mg-8.5 Al-0.5 Zn-0.2 Mn). Etched 5 Seconds in Glycol Etchant. $\times 250$.

point of this eutectic is lowered in proportion to the amount of dissolved zinc present in it, and since zinc tends to segregate in the final portion of the melt during the freezing process because of its slow diffusivity in the $\alpha(\text{Mg})$ phase, the melting point of this eutectic may fall as low as 685 degrees Fahr. (363 degrees Cent.) in some cases. Conversely, the melting point of this eutectic constituent is raised when the zinc concentrated in it by the freezing process is diffused away into the surrounding zinc-poorer $\alpha(\text{Mg})$ regions. This, then, explains the reason for the step heat treatment: (a) to utilize throughout each period of the heat treatment the highest possible temperature which is consistent with the principle of preventing the eutectic constituent from melting, in order to make the entire period of the heat treating cycle as short as possible, and (b) to increase this heat treating temperature just as rapidly as the melting point of the eutectic constituent is elevated by the process of zinc diffusion from it into the surrounding $\alpha(\text{Mg})$ regions.

Since the zinc content of the "eutectic" is not the same in every casting, i.e., the conditions of segregation may vary in individual castings, the minimum solution heat treating cycle required to eliminate completely the possibility of melting the "eutectic" will vary accordingly. Furthermore, since a solution heat treating cycle which would be completely safe for the worst conditions of segregation would be prohibitively long, a series of commercially practical solution heat treatments have been developed to cover the average conditions. In these commercial cycles the eutectic may melt in individual instances, but it has been proved that if the furnace atmosphere contains 0.5 per cent SO_2 , this SO_2 provides additional protection against "burning" (11).

Precipitation Heat Treatment—Precipitation heat treatment, or aging, increases the yield strength and hardness, leaves the tensile strength essentially unaffected, and decreases the ductility. The extent to which these changes are affected is determined: (a) by the temperature selected for aging, which, in turn, determines the form in which the precipitation appears, and (b) by the period of holding at this temperature, which determines the extent to which precipitation occurs. Moderate and high temperature aging leads to a lamellar form of localized precipitation which progresses from the grain boundaries; this lamellar form may become coarsely spheroidized with long holding times in the higher temperature ranges. Low temperature aging produces a fine globular form of general precipitation

throughout the entire grains. However, this transition from one form to the other is not sharply defined, and it must be considered as a qualitative rather than quantitative distinction. Since low temperature aging to produce the fine globular form has not been found to induce any unique properties, and since the aging periods required for its formation are prohibitively long, only the lamellar form is of practical commercial importance.

Figs. 18 and 19 show respectively the typical commercial aged conditions for the cast Mg-9Al-2Zn-0.1Mn, and Mg-6Al-3Zn-0.2Mn alloys.

While the wrought alloys usually are not solution heat treated after working because of their tendencies to grain growth, their physical condition does correspond roughly to the solution heat treated state if the preheating before working has dissolved the β (Mg-Al) constituent and if they have been cooled rapidly from the working temperature. In this condition they, too, can be aged to develop improved physical properties. Fig. 20 shows the typical structure of an extruded and aged Mg-8.5Al-0.5Zn-0.2Mn alloy.

Appendix

POLISHING MAGNESIUM ALLOYS FOR METALLOGRAPHIC EXAMINATION

The following procedure has proved satisfactory for polishing magnesium alloy specimens for routine metallographic examination:

Grinding—The grinding is accomplished by the successive use of Aloxite Cloths No. 50, 100, 180, and 240, and of emery papers No. 0 and 3/0.

Polishing—Two rotating wet laps are used, both being covered with Vel-Chamee cloth. A distilled water suspension of commercial 600 alundum is employed on the first wheel; the cloth is maintained just moist enough to prevent seizure of the specimen. The speed of this lap is from 400 to 600 revolutions per minute and the specimen is rotated counter to the wheel until the scratches from the preceding 3/0 emery are removed.

For use on the final lap, a suspension of releveligated alumina is easily prepared by thoroughly shaking a commercial grade of

levigated alumina with distilled water and then syphoning off that portion which has been allowed to settle quietly at least 3 hours per inch. Filtered soap solution is added to this suspension in the ratio of about 20 ml. per liter of suspension. Too much soap on the final wheel leads to staining of the specimen surface. The speed of this wheel is from 100 to 400 revolutions per minute, and the specimen is revolved slowly counter to the wheel until a clear, polished surface is obtained. The polished specimen is then washed quickly in running water, rinsed in acetone or alcohol, and dried in an air blast.

Throughout the entire polishing procedure it is advisable to prolong each individual grinding and polishing step to approximately double the time actually required to remove the preceding scratches in order to remove the layer of distorted surface metal as well. If this rule has been followed, it is then possible, and practical, to remove the remaining worked surface metal in the final operation by employing an alternating light etching and light repolishing technique.

An alternate method of polishing chemically (6), while not yielding quite as clear detail as the mechanical method, is, nevertheless, frequently satisfactory for routine examinations. This method consists of swabbing the specimen, which has been ground with 3/0 emery paper, with a solution of about 15 per cent HNO_3 in alcohol. The time required is usually from 30 to 60 seconds. Subsequent to this polishing treatment, the specimen is etched as usual.

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DISCUSSION

Written Discussion: By N. M. Briskin, Magnesium Foundry Laboratory, Ford Motor Co., Dearborn, Mich.

The authors have here condensed and presented information for which the magnesium industry has felt a growing need.

On the subject of microporosity, the authors say, "This defect is caused by lack of proper feeding: The last portion of the melt, i.e., the aluminum-rich portion of approximately eutectic composition, has failed to *feed* into the shrinkage cavities around the primary magnesium dendrites". It has been our experience that lack of "feeding," as the term is used in conventional foundry terminology, is not always the cause of microporosity, or microshrinkage, as the phenomenon is also known. The authors are correct in stating that "this defect can be eliminated to a great extent by proper foundry practice and design of the molds," but they imply by the term "lack of feeding" that the use of larger and heavier risers at the area showing microshrinkage is the solution to the difficulty. This conception of the cure for microshrinkage is quite prevalent in many foundries making magnesium castings, and the authors' explanation might be construed to encourage the use of this faulty remedy.

"Feeding," the term commonly applied to the sinking (due to gravity) of fluid liquid metal from risers and gates into the casting, will eliminate "surface shrinks" but our experience has shown that such feeding is not a cure for microshrinkage, or voids between the grains. As a matter of fact, in many cases, larger risers have increased rather than decreased the microporosity in thin sections below or adjacent to these large risers.

The authors imply that these voids between the primary dendrites form throughout the casting when poured, and are then filled by "feeding" of the aluminum-rich portions of the melt from heavy sections, risers and in-gates. If this were the case, then thin sections adjoining heavy ones, or directly beneath heavy risers, or in front of gates admitting large volumes of metal would rarely ever show microshrinkage. Experience has shown that the opposite is true and that such areas are sometimes the most troublesome with respect to microporosity. Furthermore, if the aluminum-rich portions of the melt could feed down in preference to the pure magnesium grains, then a chemical analysis taken at various portions of the casting would show a higher aluminum content directly beneath risers and heavy sections and front of the in-gate. Experience has shown that this is not the case.

Our experience has led us to believe that microporosity in magnesium

alloys is not caused by a difference in volume contraction of the lower melting constituents and the primary dendrites, as is commonly believed, nor that it is a lack of feeding of liquid metal, as the authors contend, but that it is a condition produced by a difference in solubility of the dissolved constituents at various temperatures. These constituents are still molten while the pure magnesium crystals begin to separate out from the solidifying melt. If the temperature is maintained for any length of time in the solidification range, these lower melting constituents may either stay dissolved in the hot metal flowing by or may redissolve in the primary magnesium crystals which have just solidified. Spot chemical analysis will not show segregation if the latter condition has taken place.

In flat thin sections, for example, which contain microporosity, an attempt to eliminate this condition by more and larger risers to "increase feeding" will result only in an increase in the amount of microporosity, especially near the base of the riser, due to the following causes: The larger risers require that a greater amount of metal flow through the casting. Most of the metal will flow along certain paths from the gate to the riser and heat up the sand in the walls of the mold along these paths. As the primary magnesium crystals begin to crystallize out in sections other than along these paths, there will be no great cause for the segregation of eutectic from these primary crystals. Thin sections will solidify soon after they are filled. Along these main flow paths, however, the continual flow of hot metal and the heating up of the sand will keep the metal flowing through this area in the solidification temperature range much longer. Less eutectic will solidify along the flow paths in the voids between the primary magnesium crystals. Instead, this eutectic will remain in solution and be carried with the hot metal going up into the riser, or may redissolve in the crystals of primary magnesium which have solidified out along the flow path. Consequently, the casting will show microporosity in patterns along the main paths of flow, and the degree of porosity will be dependent upon the amount of metal flowing through and its temperature.

Alloys with a higher aluminum content do not show as great a tendency to the formation of microporosity because of the greater amount of aluminum-rich constituents which will precipitate out at higher temperatures instead of remaining dissolved in the matrix.

The elimination of microshrinkage is not a simple problem. We believe that the solution to it lies, not in "feeding" alone, but in the proper arrangement of gates, risers and chills and control of metal temperature and pouring time to fill the mold so that a *progressive solidification* of the casting will take place, beginning, theoretically, with a point farthest from the gate.

Written Discussion: By W. Bonsack, chief metallurgist, The National Smelting Co., Cleveland.

I congratulate the authors for their excellent work in giving to the industry a comprehensive encyclopedia of the macro- and microstructures of commercial magnesium alloys. It will be a great help for many newcomers in the field of magnesium alloys to be able to refer to this paper as a guide in their work in determining the qualities of magnesium alloy products.

There is, however, one suggestion which I would like to make in regard

to the descriptive matter, and that is the use of the Fink and Willey method of nomenclature. It occurs to me that this method, although useful in some cases, is unnecessarily complicated. In this particular paper, the authors discuss at length the magnesium-aluminum constitutional diagram. They state that in most commercial magnesium alloys aluminum is the main alloying element. Magnesium forms with aluminum a compound which in the universal technical literature is known as Mg_4Al_3 . The authors prefer to call this compound β (Mg-Al). It seems to me now that this term or form is not pronounceable and does not aid in the clarification of problems. Most engineers studied chemistry at some time, and therefore know that NaCl is one atom of sodium combined with one atom of chlorine, that Al_2O_3 is two atoms of aluminum and three atoms of oxygen, etc. If we would begin to speak about β (NaCl), we would not improve the terminology, especially since this manner of formulation is not pronounceable and even less descriptive.

Returning to the case of magnesium-aluminum alloys, I would be agreeable to use such a terminology if a very unstable, undeterminable compound would have been formed. But, fortunately, the world's foremost metallographers like Hanson, Gaylor, W. Hume Rothery, Kurnakow and others agree that the composition of this compound is Mg_4Al_3 . This term means four atoms of magnesium are combined with three atoms of aluminum, and it gives very definite information about the composition of the compound easily understood by any person who ever had become acquainted ever so lightly with chemistry. I will grant that this composition might not be absolutely correct due to the fact that an extensive field of solid solubility exists at this particular concentration, but in practical use to the engineer it will not make much difference whether the aluminum content of this compound varies 1 per cent to either side, whether it is 44.487 per cent aluminum or 44 or 45 per cent. The fact remains that the investigations of the constitution of magnesium-aluminum alloys have revealed that at about 44.5 per cent aluminum, a single phase exists which can be calculated to be Mg_4Al_3 .

The discussion of zinc in magnesium alloys containing aluminum is made even more complicated. It states, "that the zinc in commercial magnesium alloys is in solid solution in the [α (Mg)-Al-Zn] and [β (Mg-Al)-Zn] and the microscopic appearance of the micro-constituent of the aluminum-magnesium-zinc alloys is similar to that of Fig. 4." Translated into simple language, I believe it means that zinc is not found in the microstructure since it is taken into solution by the magnesium-aluminum solid solution and by the compound Mg_4Al_3 . The structure is similar to the one shown in Fig. 4.

I would like to bring out the point that we must not complicate matters unnecessarily at any time, and especially not at the present, where we must not lose precious time trying to figure out what is meant by a complicated formula. From β (Mg-Al) one cannot calculate the chemical composition of the compound while from Mg_4Al_3 , even though it might not be absolutely correct, one is able to do so.

Written Discussion: By W. E. McCullough, chief metallurgist, Bohn Aluminum & Brass Corp., Detroit.

We wish to congratulate Messrs. Hess and George on their most inter-

esting and comprehensive report covering the metallography of commercial magnesium alloys. Their description of the polishing and etching methods used on these alloys is excellent, and their identification and description of the microconstituents is self-explanatory. Their report cannot but help to be of the greatest assistance to anyone dealing with the metallography of the mentioned magnesium alloys.

One point that might be interesting at this time is the relationship between the microstructure and the mechanical properties of magnesium alloys. We shall illustrate with Dowmetal "H" (Magalloy X-7).

Test bars were cast of Dowmetal "H" (Magalloy X-7) in green sand molds from one heat of metal having a chemical analysis of:

	Per Cent
Aluminum	6.17
Zinc	2.78
Manganese	0.32
Magnesium	Remainder

The bars were used to obtain mechanical properties and photomicrographs.

The bars were divided into three groups as follows:

Group I—Condition—As Cast
Group II—Condition—Solution Heat Treated
Group III—Condition—Solution and Precipitation Heat Treated

Characteristic mechanical properties were as follows:

	Tensile Strength P.S.I.	Yield Strength P.S.I.	Elongation Per Cent in 2 Inches	Brinell 500/10/30
As Cast (Group I)	28,000	19,400	5.5	50.3
Solution Heat Treated (Group II)	40,000	19,200	14.5	53.4
Solution and Precipitation Heat Treated	39,200	23,400	6.0	60.5

Photomicrographs were made of the structures of the bars from each group as illustrated in Figs. A, B and C.

From correlation of the microstructures and mechanical properties, proper control of heat treatment can be maintained and Messrs. Hess and George have provided an excellent instruction to those desiring to make use of such heat treatment control.

Written Discussion: By Allen M. Montgomery, Aluminum Research Laboratories, Aluminum Company of America, Cleveland.

The authors are to be congratulated on their very timely paper. It should prove quite useful as a guide to metallographists unacquainted with magnesium and its alloys.

We have used a macroscopic etch for some time which has proven quite satisfactory for the magnesium-aluminum and magnesium-aluminum-zinc casting alloys in developing grain size. This is similar to the authors' phospho-pical etch except that acetic acid is the active agent. It consists of:

Glacial acetic acid	5 ml
Picric acid	6 grams
Ethyl alcohol	85 ml

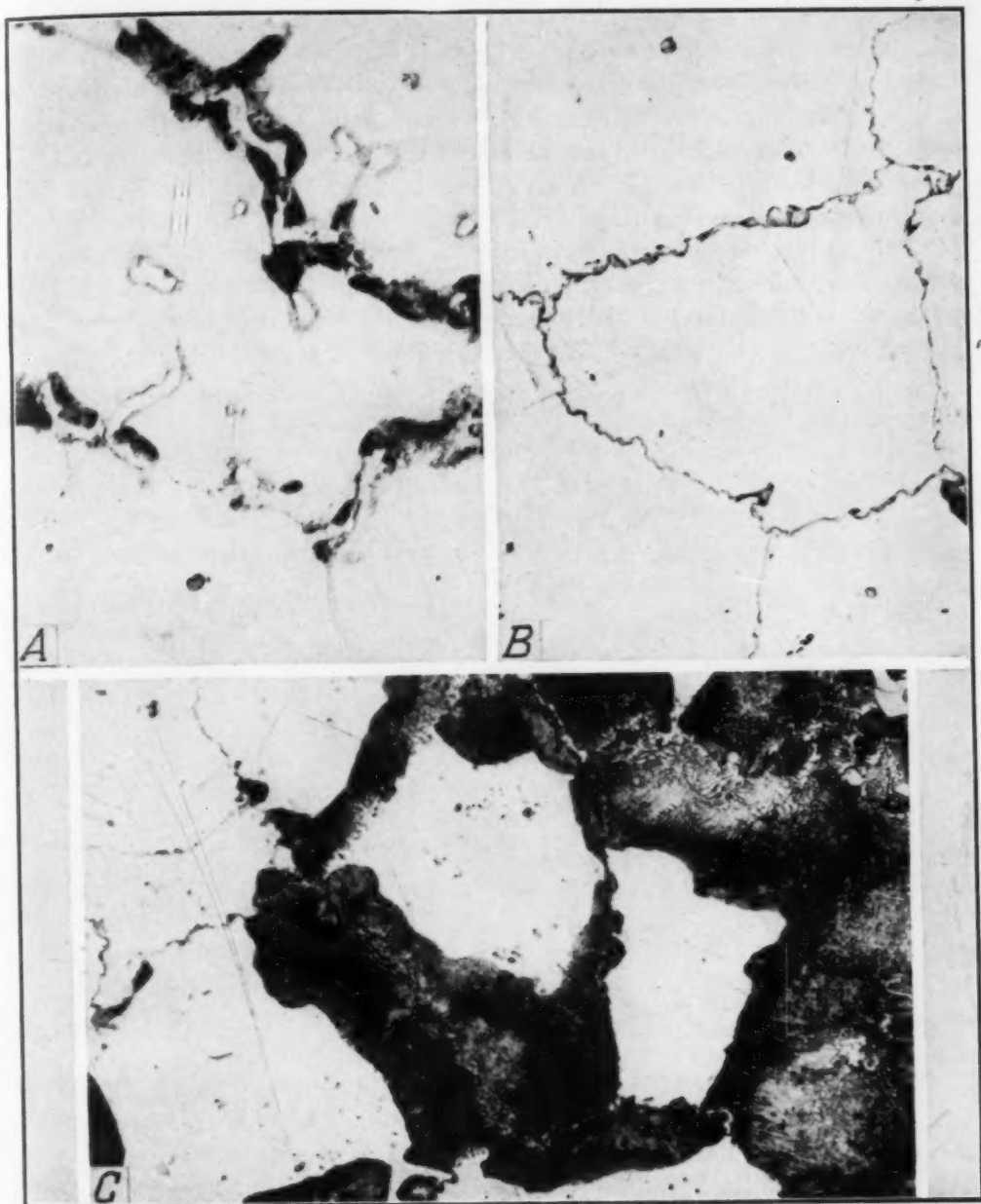


Fig. A—Bar From Group I. The Photomicrograph of the "As Cast" Bar Showed Both the Massive Clear White $\beta(\text{Mg-Al})$ Areas and the Lamellar Form of the Same Phase. Several Manganese Particles were also Present. $\times 250$.

Fig. B—Bar From Group II. The Photomicrograph of the "Solution Heat Treated" Test Bar Revealed the Typical Microstructure Expected After this Type of Treatment. There Were Also Manganese Particles and Magnesium Silicide Present. $\times 250$.

Fig. C—Bar from Group III. The Photomicrograph of the "Solution and Precipitation Heat Treated" Test Bar Showed the Typical Microstructure, Heavy Massive Areas of the Lamellar Form of the $\beta(\text{Mg-Al})$ Phase. Magnesium Silicide and Manganese Particles Were Also Present. $\times 250$.

Denatured alcohol may be used instead of ethyl in which case about 15 ml. of water must be added. This etch works best, as do most macroscopic etches, when the material is in the solution heat treated condition rather than in the as-cast or solution treated and aged conditions. This is an immersion etch

requiring a surface prepared by polishing through the metallographic papers and through a broadcloth or duveteen wheel with 600 alundum powder. The surface is covered with the etching solution and is rocked back and forth to spread the etching solution. Etching does not begin until the solution becomes a beet red. The solution should be kept on the sample and renewed until the grain structure appears. The etch should be made up fresh each time as it appears to deteriorate on standing.

I doubt whether most metallographists would share the authors' expectation that the microstructures of commercial magnesium-aluminum alloys should consist of cored, primary α (Mg) dendrites and a eutectic composed of α (Mg) and β (Mg-Al) (by which I assume they mean a pearlitic type of eutectic). While I have no explanation to offer, it should be pointed out that in eutectic systems where the eutectic composition has a lamellar structure, the alloys near the α solid solution containing a small amount of eutectic usually have that eutectic present as massive particles rather than as small amounts of lamellar material. The aluminum-copper system is an excellent example of this. Portevin and Brady have both commented on the rareness of the true lamellar structure in eutectics.

Admitting that no very satisfactory explanation of the massive and "divorced" appearance of such eutectic structure exists, nevertheless it appears doubtful whether much is added by the authors' explanation. Undercooling is always associated with very fine constituents rather than the coarse, macroscopic particles of β (Mg-Al) which may be obtained on slow cooling of commercial alloys. Also, no evidence of undercooling is reported in the literature. On the other hand, in die castings where a very rapid quench (and therefore very little opportunity for diffusion and coalescence) obtains, the β (Mg-Al) constituents are still in a massive form as illustrated in Fig. 11 of the paper.

The use of the word "primary" in describing the β (Mg-Al) constituent would appear to be somewhat unfortunate. In no sense of the word can this constituent be described as primary, at least in commercial alloys. The α magnesium solid solution dendrites must be primary in the sequence of solidification.

In the preparation of magnesium alloy samples for microscopic examination, we use only No. 120 emery cloth, No. 1 and No. 3/0 emery papers. These are mounted on a polishing wheel to eliminate slow hand polishing. On the second wheel we use black duveteen cloth with a tap water suspension of 600 alundum. The last wheel is a fine silk velvet on which we make a paste of Merck's heavy MgO with distilled water. The MgO is sifted through a 100-mesh sieve, but is not prepared in any other way. To dry the sample off, it is simply held under the hot water tap for a moment and any water which clings to the polished surface is blown off. With this preparation it is possible to get scratch-free surfaces which are free of twinning and distorted constituents indicating worked metal.

Written Discussion: By R. L. Heath, chief metallurgist, Allison Division, General Motors Corp., Indianapolis.

The authors are to be complimented on a valuable addition to the metallography of commercial magnesium alloys. The available literature on this

subject is not very voluminous and such additions are indeed welcome.

The photomicrograph in Fig. 11 of the die cast Dowmetal R shows a massive formation of the primary β (Mg-Al) phase. Under such a rapid cooling rate, the writer is inclined to believe that the primary β (Mg-Al) phase is the result of undercooling and the subsequent formation of the hypereutectic rather than a coalescence of the eutectic. It is doubtful that coalescence of the eutectic would take place under such a rapid cooling rate.

Fig. D is a photomicrograph of Dowmetal C at $\times 100$ showing a continuous network of primary β (Mg-Al)-Zn constituent after solution and aging heat treatments have been completed. The amount of this constituent varies with like castings from different heats. The effect of zinc concentration on the

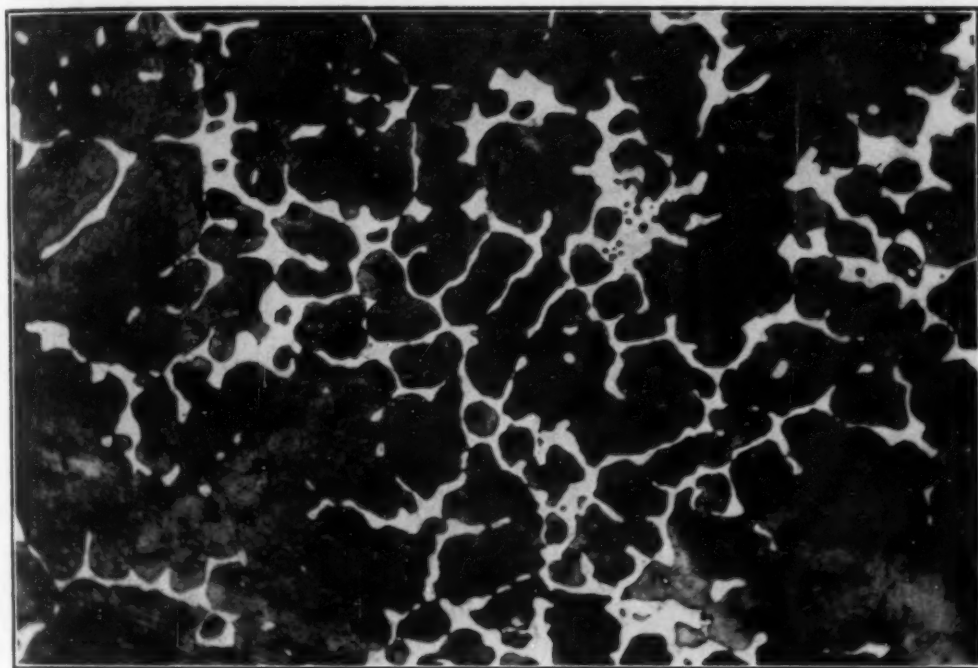


Fig. D—Photomicrograph of Dowmetal C (Mg-9Al-2Zn-0.1Mn) Showing a Network of Primary β (Mg-Al)-Zn Phase After Solution and Aging Heat Treatments. Etched 5 Seconds in 2 Per Cent Tartaric. $\times 100$.

diffusibility of the eutectic would explain these variations in the amount of primary phase after solution heat treatment has been completed. It has been our experience that a structure of this type results in a brittle material and is undesirable in highly stressed sections.

Work that we have carried out is in agreement with your results that show the formation of the coarser lamellar form of precipitate at higher aging temperatures. We have also found that a decrease in tensile strength and hardness accompanies the formation of the coarse precipitate at higher aging temperatures. It would be interesting to see its effect on the other mechanical properties, mainly the fatigue endurance limit.

Written Discussion: By R. E. Ward, assistant chief metallurgist, Eclipse Pioneer Divisions, Bendix Aviation Corp., Bendix, N. J.

This excellent paper was reviewed carefully and all etchants were tried out since several were new to our laboratory.

From the results of our tests of the etchants as described in the paper, we have found the following etchants for micro-examination to be the best for the particular heat treatment noted. The time of etch shown is what we believe to be the best. All etching solutions were used at room temperature. The 6 per cent aluminum-3 per cent zinc magnesium alloy was used for all tests. (Dowmetal H and AM 265).

Condition	Etchant	Time of Etch
As Cast	"Glycol"	2½ seconds
Age Only	"Glycol"	5 seconds
Solution Treated	"Phospho-picral"	25 seconds
Solution Treated and Aged	"Phospho-picral"	2 seconds

In macro-examination when finishing with No. 240 abrasive belt, the time of etching was 30 seconds while a 15-second etch appeared to be sufficient when the specimen was finished on 3/0 metallographic paper. Polishing with No. 240 abrasive belt is satisfactory for a quick examination using the acetic acid etchant, but it was necessary to use 3/0 metallographic paper for good definition with tartaric acid etch.

Macroetching without removing the reaction products gave excellent results when using the tartaric acid etch. This was not true of the acetic acid etch.

This paper has been prepared in an excellent manner and presents to industry, techniques which will add greatly to the study of magnesium alloys and the proper interpretation of the heat treatment.

Written Discussion: By S. J. Broderick, metallurgical unit, Materials Laboratory, Experimental Engineering Station, Army Air Forces, Wright Field, Dayton, Ohio.

The authors are to be congratulated for a most needed and timely paper on the appearance of microstructural constituents in magnesium alloys. This paper will be of much value to the constantly expanding number of workers in the magnesium industry. It is hoped that more papers of a research nature will be forthcoming from the laboratories now engaged in magnesium investigation.

The lamellar precipitated constituent, as illustrated in Fig. 4, is a fine example of an ideal structure. Such a microstructure, however, may be difficult to find in commercial castings. Photomicrographs made in this laboratory, two of which are included, Figs. E and F, of the lamellar precipitated constituents are not so well defined as the authors' example, but are what one may expect to find in routine examinations of castings.

More photomicrographs of microporosity and burning would be desirable, as it is frequently difficult to distinguish between these two defects. Microporosity may vary widely from small angular breaks at the grain boundaries to large circular voids. If the microshrinkage voids are large they may have the appearance of a bad case of burning. Fig. G is an illustration of a severe case of microshrinkage porosity in which the large voids in the center, if present alone in a small section, could be mistaken for burning. Generally

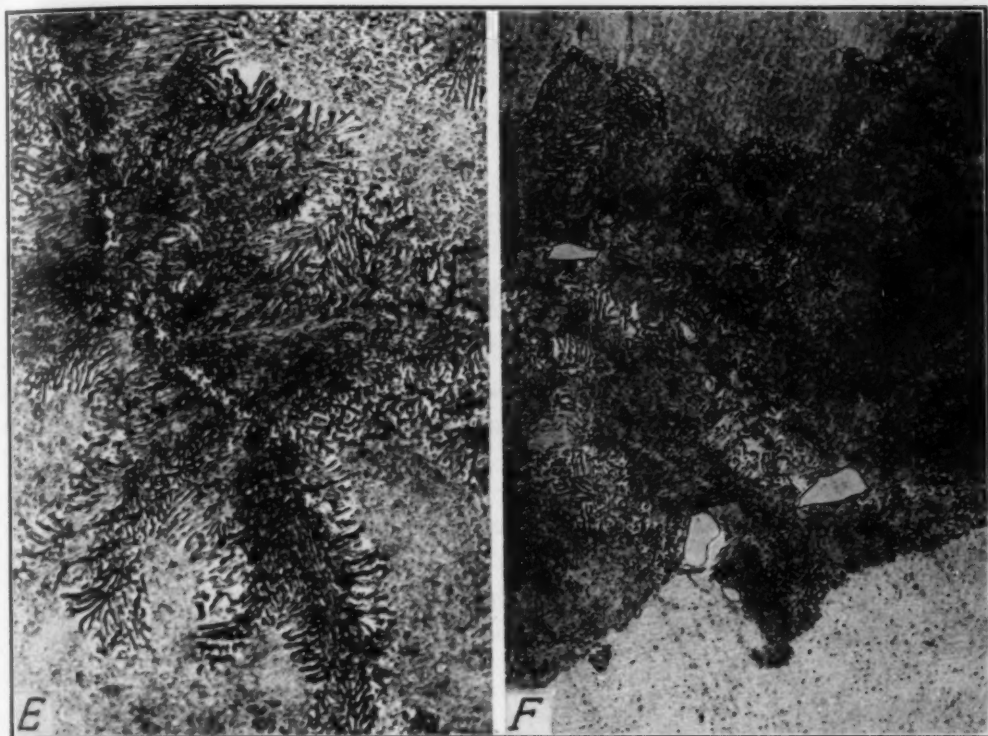


Fig. E—Lamellar Precipitate in Heat Treated and Aged AM 265 Alloy. Glycol Etch. $\times 500$.
Fig. F—Lamellar Precipitate in Heat Treated and Aged Dowmetal C Alloy. Glycol Etch. $\times 500$.

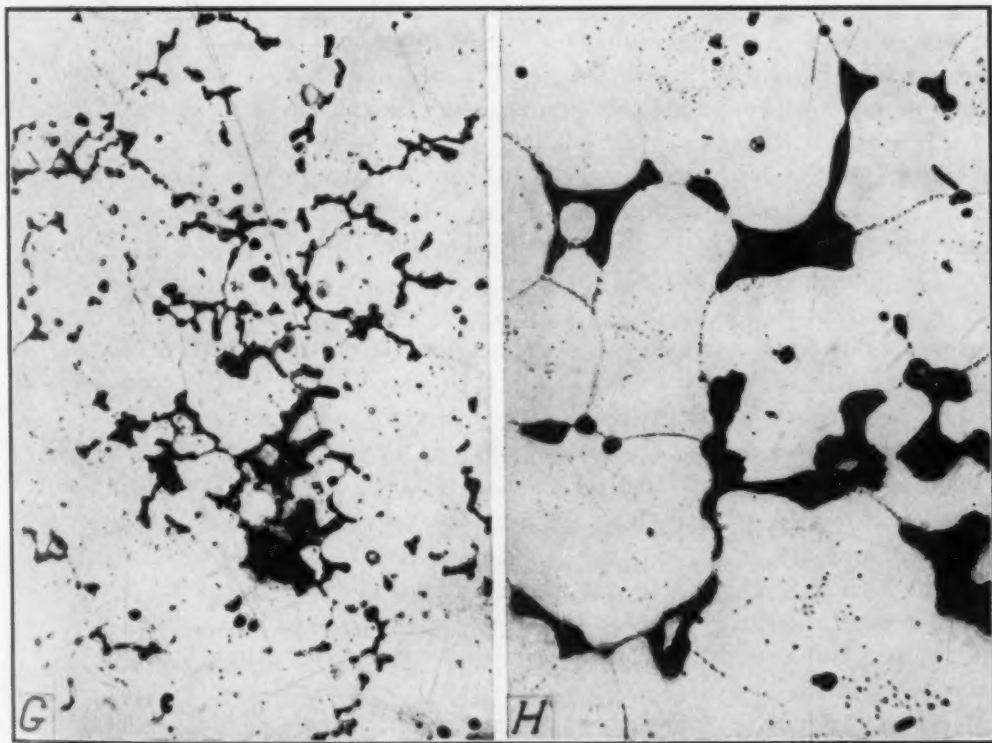


Fig. G—Characteristic Form of Microshrinkage. Etched in Glycol. $\times 100$.
Fig. H—Burning. Solution Temperature Too High. Etched in Glycol. $\times 100$.

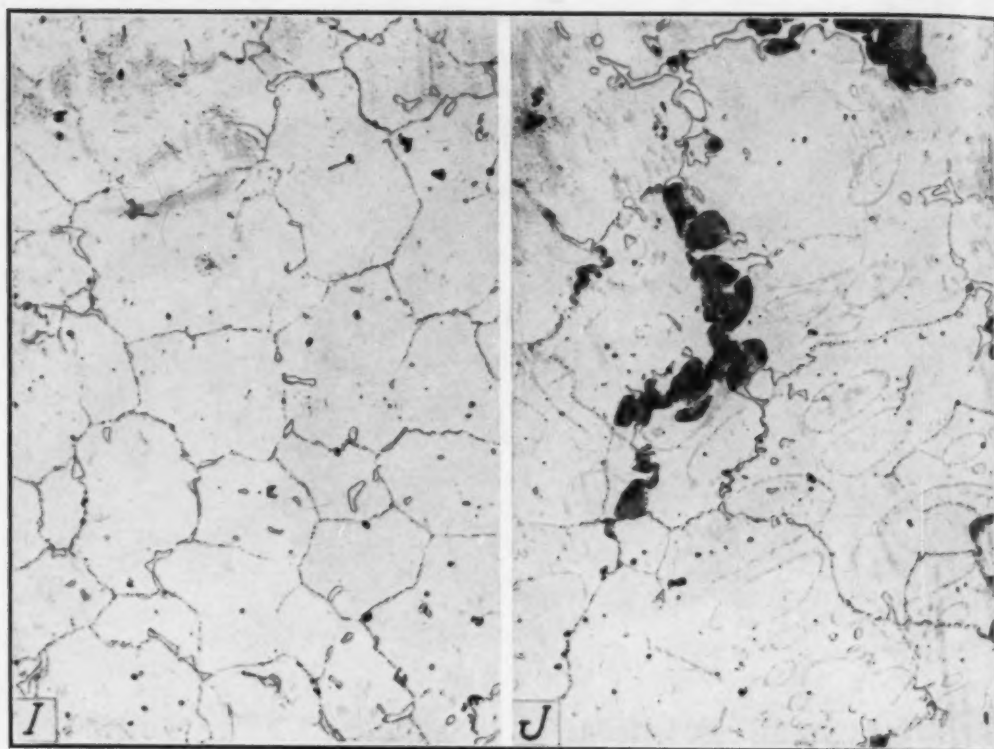


Fig. I—Insufficient Heat Treatment in AM 260 Alloy. Etched in Glycol. $\times 100$.

Fig. J—Insufficient Heat Treatment in Dowmetal C Alloy. Etched in Glycol. $\times 100$.

in severe cases of microshrinkage porosity there will be some evidence of the fine angular breaks at the crystal boundaries so that it is possible upon close examination to differentiate between microshrinkage and burning. An example of a bad case of burning is shown in Fig. H and is included to illustrate what happens if the solution treatment temperature is too high. The small black areas in the photomicrograph, Fig. H, depicting burning, appear to be thicker and more rounded than the microshrinkage voids.

Continuing a few more remarks on microshrinkage it is well to remind the reader that if microshrinkage porosity is present in small widely scattered areas, it will have an insignificant effect upon the mechanical properties, but if the porosity is localized and in an aggravated form, then it can seriously affect the properties. Consequently good foundry practice would stipulate the elimination of microshrinkage porosity in the stressed parts of the casting, and if necessary, allow it to form in the lightly stressed sections, and this can be accomplished by proper manipulation of the usual methods of gating, chilling and riser systems.

Insufficient solution heat treatment, either by too low a temperature or too short a time, does not produce the maximum mechanical properties. Such a condition may be recognized in a microscopic examination by the white colored angular primary constituent, the β (Mg-Al) compound not completely dissolved in the matrix. Since the authors did not include in their paper photomicrographs of insufficient solution treatment, Figs. I and J are shown, simply for general information.

Authors' Reply

Mr. Briskin's observation that in many cases the use of larger risers has increased rather than decreased the microporosity in thin sections below or adjacent to such risers is certainly true. This effect can be explained in the following manner: The larger risers require that a greater volume of metal must flow through the mold, and the passage of this greater volume of metal heats up the sand in the mold along the paths of flow, just as Mr. Briskin has pointed out. The heating of the mold walls may be expected to be most severe where the volume of metal flow has been the greatest. In such a section the subsequent freezing of the metal is delayed. If it is delayed until all adjoining sections have solidified, then microporosity will form in this section because the volume contraction of the liquid upon solidifying leads to cavities which can no longer be "fed".

We did not intend to imply by our term "lack of feeding" that the use of larger and heavier risers at the area showing microporosity is a complete solution to the difficulty. On the contrary we meant the term to include any mechanism, for example, non-progressive solidification, which prevents the last aluminum-rich portion of the melt from feeding into the shrinkage cavities around the primary α (Mg) dendrites which are the result of the volume contraction of the melt in solidifying.

Areas containing microporosity show a lower aluminum content than is average for the casting. This fact is most clearly demonstrated in Figs. K and L which show photomicrographs of an area of microporosity in a sand cast Mg-9 Al-2 Zn-0.1 Mn alloy. This casting was partially solution heat treated and then aged. The micrograph shows definitely that less precipitation has occurred in the regions of microporosity, and hence that the supersaturation in these regions before aging was lower than normal, i.e., that the aluminum content of these regions is subnormal. This is the best proof that the final bit of aluminum-rich melt of eutectic composition was prevented from feeding into these regions.

Mr. Bonsack's comment that even approximate formulas for the composition of intermetallic phases have a definite value is certainly warranted. We should have indicated that of the various formulas used to describe the β (Mg-Al)— Mg_3Al_2 was proposed by Hanson and Gaylor; Kurnakow assigned the formula Mg_4Al_3 , which in turn has been used by Köster; while Laves, Löhberg and Rahlfs have shown it to be $\text{Mg}_{17}\text{Al}_{12}$ —we prefer to accept the $\text{Mg}_{17}\text{Al}_{12}$ designation since this was fixed on the basis of a determination of the crystal structure.

Mr. McCullough's contribution requires some comment since the properties shown are not typical of those that may ordinarily be expected in commercial production. While the combination of properties listed is not unusual and is occasionally obtained from chance melts, the fact that the indicated yield strength is high in every group leads to the supposition that some other criterion than the standard 0.2 per cent offset method was used in selecting the values for the yield strengths. Typical values for the yield strength (0.2 per cent offset) of "H" alloy would be: 11,550 pounds per square inch for the "as

cast" condition, 12,200 pounds per square inch for solution heat treated, and 18,400 pounds per square inch for solution and precipitation heat treated.

Both Mr. Montgomery and Mr. Heath have commented upon the "divorced" appearance of the structure of the eutectic between α (Mg) and β (Mg-Al) as it appears in the commercial magnesium alloys. Since this paper was written, a satisfactory explanation for this phenomenon has been derived which requires no such hypothetical and questionable mechanisms as undercooling or coalescence. Furthermore, since these "divorced" eutectics appear in other alloy systems, and since no satisfactory explanation is explicitly recorded in the literature, it seems worthwhile to detail the explanation here.

First of all, metallographic examination shows that the "divorced" appearance is not encountered in high purity binary alloys but only in polynary alloys. The binary eutectic structure, defined in the sense used by Portevin as an intimate mixture of the crystals of two phases where the size of the crystals are very small compared to the general macrostructure, is the result, according to the phase rule, of the simultaneous crystallization of these two phases at a constant temperature. However, in a polynary alloy the simultaneous crystallization of two phases from a melt does not occur at a constant temperature, again according to the phase rule, but can occur during a falling temperature within the limits of the particular phase field of the reaction. In such a simultaneous crystallization process the size to which the individual crystals grow is governed by the actual cooling rate and the relative rates of nucleation and growth of the two phases. Thus the process of the simultaneous crystallization of two phases from the melt in a polynary alloy is exactly analogous to the crystallization of a single phase from the melt in a binary alloy and may, depending upon the actual cooling rate involved, lead to a few large crystals or to numerous small crystals. In the particular case of the commercial magnesium-aluminum-zinc alloys under discussion here, it is apparent that most commercially encountered cooling rates lead to massive crystals, even, for example, during the cooling of a die casting (Fig. 11), and that drastic quenching is required to produce small crystals (Fig. 9). Furthermore, it is interesting to note that even in the case of the drastic quench illustrated (Fig. 9) that only the α (Mg) phase has formed small crystals while the β (Mg-Al) has still formed only one continuous crystal.

Abnormal segregations of the β [(Mg-Al)-Zn] phase, such as is illustrated by Mr. Heath's example, tend to occur at the surfaces of chills and are a direct result of the high local cooling rate in intensifying inverse segregation.

Some studies of the effect on fatigue strength of aging at a higher temperature have been carried out in this laboratory. The evidence to date has not shown any great difference between this treatment and the usual aging treatment.

Mr. Ward indicates that he finds phospho-picral used for 2 seconds to be the best etchant for specimens in the solution heat treated and aged condition. This is somewhat contrary to our experience since we find that with continued use, as when a number of specimens are etched successively in the same dish of etchant, that phospho-picral does not give consistent results with short period etching, while longer periods of etching obliterate or mask the detail present in the microstructure.

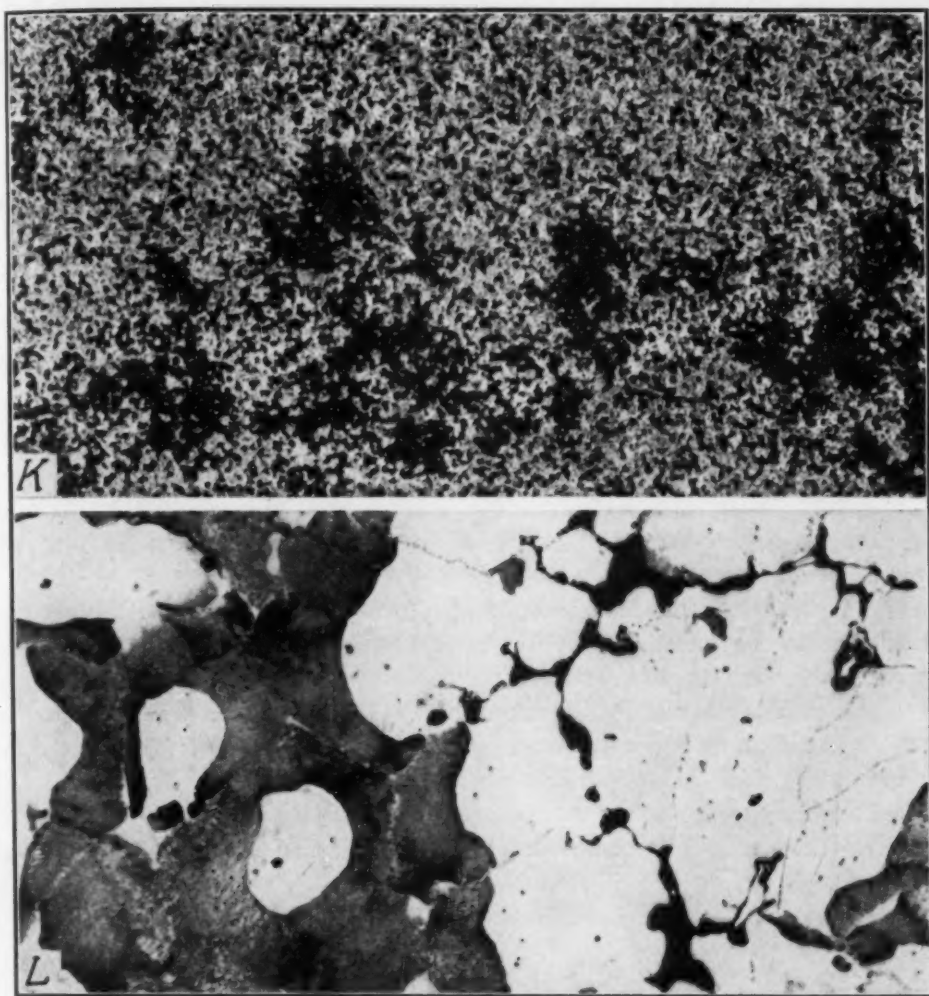


Fig. K—Macrograph of Area Containing Microporosity in a Commercial Dow-metal C (Mg-9Al-2Zn-0.1Mn) Sand Casting. The Casting Has Been Partially Solution Heat Treated and then Slowly Cooled. The Dark Areas Show the Absence of β (Mg-Al) Precipitation. Etched 10 Seconds in Glycol. Oblique Illumination. $\times 5$.

Fig. L—Micrograph of Same Specimen as Fig. K, Showing that the Areas Not Exhibiting Precipitated β (Mg-Al) Are the Areas Containing the Microporosity Voids. Etched 10 Seconds in Glycol. $\times 100$.

In general we recommend "glycol" etchant for securing maximum detail for general metallographic study of any magnesium alloy specimen regardless of its condition. The acetic-glycol etchant is a stronger etchant and gives somewhat less detail than plain "glycol", but its use is frequently required with wrought or solution heat treated material in order to develop the grain structure. It should not be used until a trial of plain "glycol" has been shown to be inadequate for a particular specimen. Phospho-picral is a special purpose etchant and is recommended only for the specific purpose of developing the maximum contrast between the massive β (Mg-Al) particles and the α (Mg) matrix for examinations to determine the completeness of solution of the β (Mg-Al) phase.

Mr. Broderick's photomicrographs E and F showing the lamellar precipitation in solution heat treated and aged castings are perfectly typical of this condition, while the lamellar precipitation of Fig. 4 is typical of the "as cast" condition, and was taken from a commercial casting.

Distinguishing between microporosity and burning is difficult in most cases. However, in some instances the shape of the voids offer some aid. "Burning" voids tend to have a smooth, concave outline, resembling the outline of the molten eutectic (Fig. 9), while microshrinkage voids tend to have the irregular outline characteristic of massive β (Mg-Al). This distinction is by no means infallible.

If the area immediately surrounding a patch of voids can be shown to be deficient in aluminum content, for example, as already shown in Fig. K, this fact is positive evidence that the voids are microporosity. However, absence of such an aluminum deficiency is not always proof for "burning".

We agree with Mr. Broderick's emphasis upon the desirability of allowing microporosity to form in the lightly stressed sections of a casting when it cannot be eliminated.

We have tried the macroscopic etchant described by Mr. Montgomery and find it to be excellent for developing grain contrast in coarse-grained material. It seems to possess no advantages over the simpler, diluted tartaric and acetic acid etchants for developing the flow lines in wrought material, nor is it satisfactory for a microscopic etch due to the severity of its attack.

The use of the term "primary" in describing the massive form of the β (Mg-Al) which appears in "as cast" material, as found in much of the American literature, is erroneous, and we prefer to call it simply massive β (Mg-Al).

STUDY OF INVERSE SEGREGATION SUGGESTS NEW METHOD OF MAKING CERTAIN ALLOYS

BY M. L. SAMUELS, A. R. ELSEA AND K. GRUBE

Abstract

Some instances of extreme inverse segregation were observed in an alloy of 50 per cent iron and 50 per cent copper. This alloy possesses a very wide solidification range and freezes as two distinct structural constituents. Iron dendrites containing some copper in solid solution begin to form at about 2625 degrees Fahr. (1440 degrees Cent.) and the copper-rich phase does not solidify until the temperature has dropped to approximately 2000 degrees Fahr. (1095 degrees Cent.).

A copper-rich skin on the lower outside surfaces of some castings was thought to have originated from interdendritic flow during the mushy stage. It was found possible, by reheating into the mushy range, to displace the low melting phase with other metals which are not miscible with iron in the molten state as, for example, silver or lead.

Other alloys which freeze over a wide range of temperature and which also solidify as two distinct constituents were investigated. Alloys of silver-nickel, silver-cobalt, beryllium-magnesium, aluminum-lead, iron-magnesium, and copper-lead were made.

Reasoning from this evidence of interdendritic flow in alloys which solidify as two distinct constituents, it is suggested that inverse segregation in alloys such as the low tin bronzes undoubtedly arises from interdendritic flow. Alloys which may ultimately show only one constituent must pass through a stage during solidification in which there are solid dendrites and connecting interdendritic channels filled with liquid rich in the lower melting constituent.

IN the course of an examination of a group of 50-50 copper-iron ingots it was found that the location in the upper central part, directly underneath the hot top, contained in some cases as little as

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. Of the authors, M. L. Samuels was associated with Babcock & Wilcox Tube Co., Beaver Falls, Pa., at the time this paper was presented, but is now with the United States Pipe and Foundry Co., Burlington, N. J., A. R. Elsea is research metallurgist and K. Grube is research engineer, Battelle Memorial Institute, Columbus, Ohio. Manuscript received January 7, 1942.

40 per cent copper. Ordinarily it is expected that the location next to the mold surface, which necessarily freezes first, will contain the greatest percentage of the high melting constituent, and that the upper central location will be richest in the low melting constituent because it is the last region to solidify. A complete chemical survey of the cross sections of several split ingots revealed the presence of an outside skin of almost pure copper.

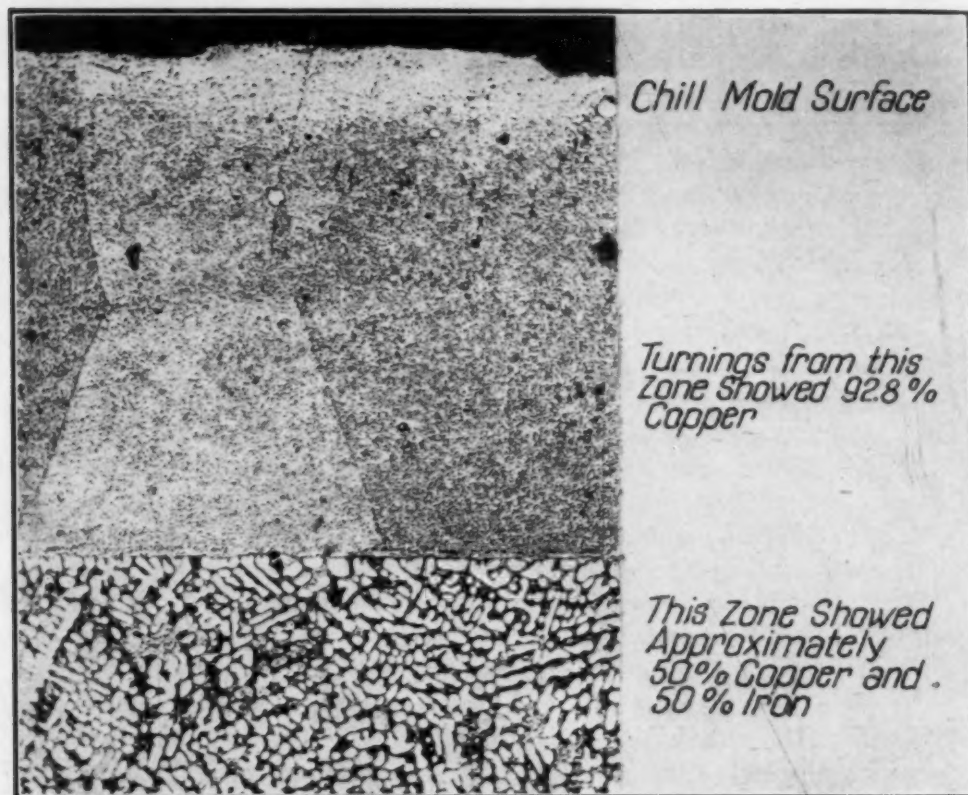


Fig. 1—Copper-Rich Layer on the Chill Cast Surface of Gear Blank Containing 50 Per Cent Iron and 50 Per Cent Copper in the Original Melt. $\times 100$.

This condition was observed again in gear blanks cast from the copper-iron alloy into a horizontal dry sand mold fitted with a metal chill ring around its circumference. The skin of almost pure copper was clearly visible to the eye on a ground cross section and turnings from the outer zone showed 92 per cent copper upon analysis. Fig. 1 illustrates the structure on the chill ring surface and shows, also, a sharp line of demarcation between the outer skin and the copper-iron base metal. The 50-50 alloy was known to be a bad actor with respect to shrinkage and hot cracking so the mold for the 6 by $1\frac{1}{4}$ -

inch gear blank was provided with a shrinkhead 4 inches in diameter and 4 inches high in order to insure adequate feeding.

The cases cited above constitute clear instances of inverse segregation, but, of course, throw no light on the mechanism by which the relatively pure copper came to be located on the outside skin where the highest melting constituent would normally be found. A study of Vaughn's (1)* review of published information on hypotheses, set up as explanations for the phenomenon, revealed at least nine theories, including: (a) the undercooling theory by Masing (2), (b) Ludwig-Soret effect propounded by Benedicks (3), (c) Le Chatelier's principle of "mobile equilibrium", proposed by Smith (4), (d) contraction-pressure theory by Kühnel (5), (e) interdendritic flow theory by Bauer and Arndt (6), (f) gas evolution theory by Genders (7), (g) crystallization pressure theory by Masing and Haase (8), and (h) the primary crystal migration theory proposed by Watson (9). Hull (10) has recently suggested that inverse segregation in brass chill castings may come from condensation and re-absorption of zinc vapor.

Most of the theories listed above do not appear adequate or comprehensible, but that suggested by Bauer and Arndt on interdendritic flow seemed to offer a satisfactory explanation in the case of the copper-iron alloy. The iron-rich dendrites were known to form in the neighborhood of 2600 degrees Fahr. (1425 degrees Cent.), whereas the copper-iron low-melting constituent did not solidify until the melt had dropped to a temperature of approximately 2000 degrees Fahr. (1095 degrees Cent.). The metal mold would by that time have expanded and the solidified dendrites of the casting shrunk, so that there would be a space between, which could be filled by the copper-rich liquid flowing through the interdendritic channels.

In an effort to test this theory, a specimen from the 50-50 copper-iron alloy was machined into the form of a tapered plug and fitted into a holder as shown in Fig. 2. It was first intended to attempt passing molten copper through the interdendritic channels, but in view of the fact that it would be hard to distinguish between the new and original copper, silver was selected. The fixture was heated to 2150 degrees Fahr., at which temperature the copper-rich liquid started to exude from the specimen. The exuded material subsequently changed to a copper-silver eutectic and then to pure silver.

*The figures appearing in parentheses pertain to the references appended to this paper.

The microstructure of the base metal, or parent alloy of iron and copper, is shown in Fig. 3, and that of the displaced iron-silver is shown in Fig. 4.

The displaced specimen was sound and entirely free of copper, except for minute particles within the dendrites which had evidently

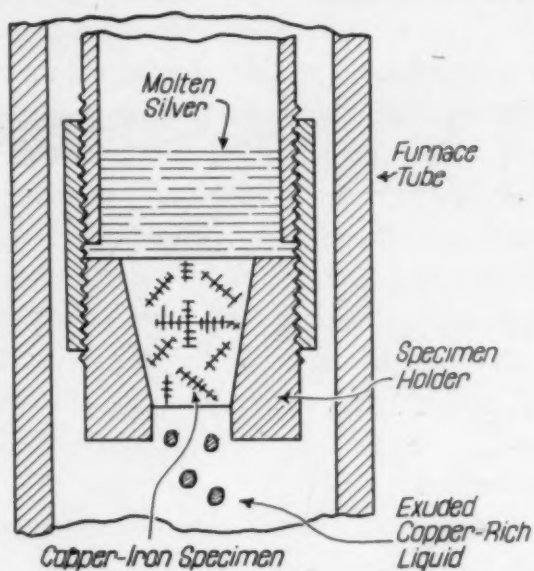


Fig. 2—Apparatus Employed for Displacing the Low Melting Phase by Another Liquid.

precipitated from solid solution upon cooling after displacement. The material showed the same structure with the exception that silver had replaced the copper-rich interdendritic material.

The success of the first experiment proved that interdendritic flow could occur, and it was suggested that perhaps alloys immiscible in the molten state could be made by selecting a suitable parent alloy and displacing the low-melting phase. A number of such alloys were made successfully, as described below.

IRON-BASE ALLOYS

The constitutional diagram of the copper-iron system shown in Fig. 5 indicates that, for compositions ranging from about 20 to 80 per cent copper, there is a temperature range of approximately 570 degrees Fahr. (300 degrees Cent.) over which the copper-rich phase is molten and exists in the interdendritic interstices. Some limitations for displacement are that the displacement metal must have a melting point well below that of the iron-rich dendrites and

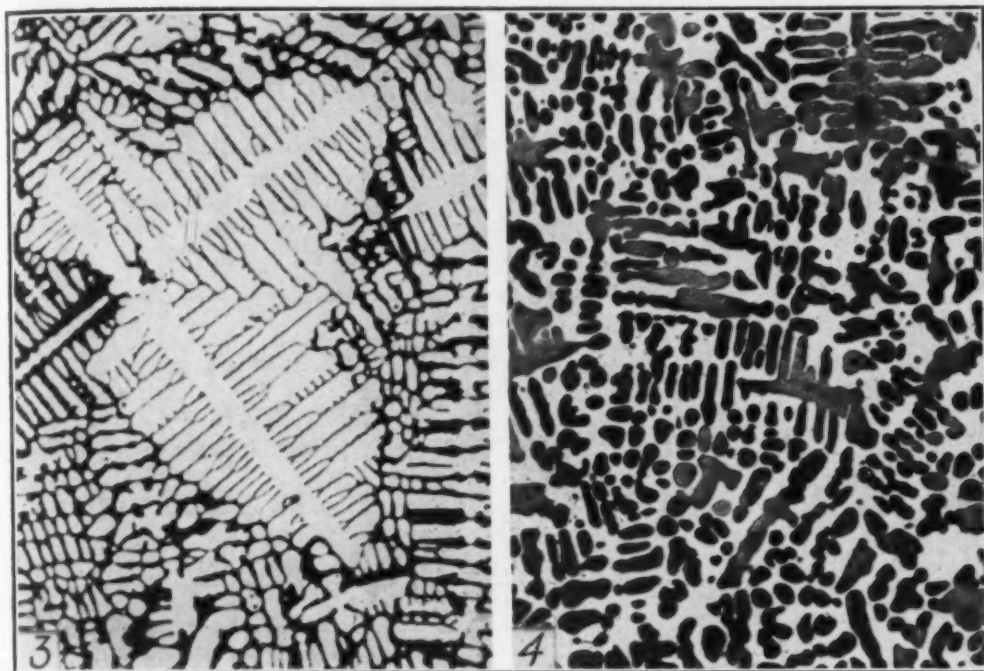


Fig. 3—Microstructure of the Iron-Copper Alloy After Heat Tinting. The White or Dendritic Material is the Iron-Rich Phase. $\times 100$.

Fig. 4—Microstructure of the Displaced Iron-Silver Alloy After Heat Tinting at a Much Higher Temperature. The Iron-Rich Dendrites Have Been Darkened, While the Silver Remains Bright. $\times 100$.

that there must be little or no solubility between iron and the displacing metal.

Iron-Silver

A 12-pound plug of iron silver was produced by displacement and rolled into plate and sheet; other portions of the plug were cold-drawn into wire. Some mechanical properties and compositions of the original and the displaced alloy are as follows:

Identification	Composition, Per Cent			Yield Strength Lb./Sq. In.	Ultimate Strength Lb. / Sq. In.	Per Cent Elong. in 2 In.	Per Cent Reduc. of Area	Bri- nell Hard- ness
	Fe	Cu	Ag					
Cu-Fe (Parent Alloy)	49.6	49.1		53,500	65,000	22.5	37.3	121
Fe-Ag (As-Rolled)	45.0	2.7	51.0	28,500	40,750	31.0	42.5	78
Fe-Ag (Annealed)	45.0	2.7	51.0	25,000	41,000	39.0	62.9	..

The 2.7 per cent residual copper apparently comes from that in solid solution within the dendrites at the displacing temperature which, of course, cannot be removed. Microscopical examination showed no interdendritic copper, but high magnification revealed the presence of small globules in the iron dendrites. Fig. 6 shows the microstructure from a small cold-drawn wire.

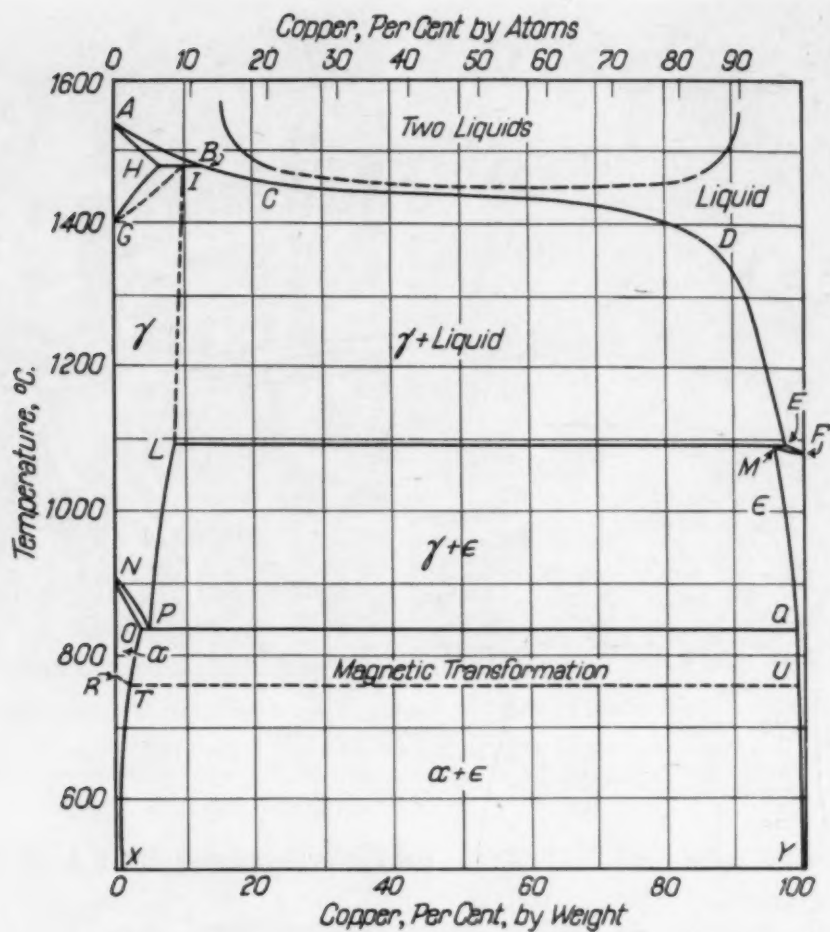


Fig. 5—(Taken from "Alloys of Iron and Copper", p. 33, by Gregg and Daniloff.)

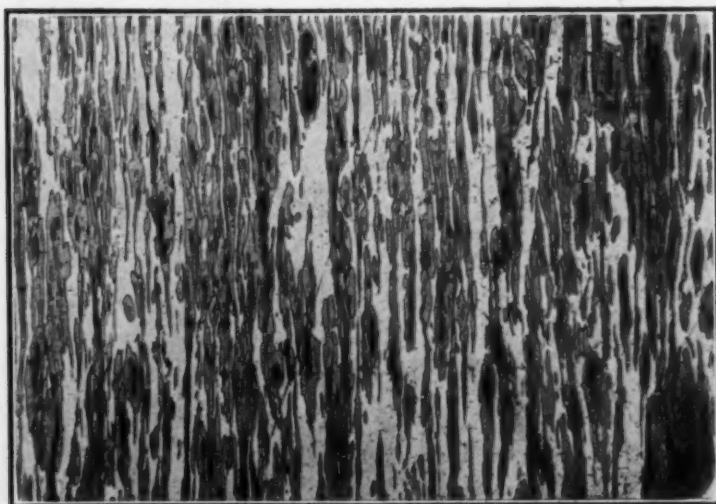


Fig. 6—Microstructure of Cold-Drawn Wire from the Iron-Silver Alloy. $\times 100$.

Iron-Nickel-Silver

A series of small melts showed that considerable nickel could be alloyed with the iron-rich phase in copper-iron alloys without destroying the dendritic structure. The results from one melt may be listed as follows:

Identification	Parent Alloy Calculated Composition in Per Cent			Displaced Alloy Actual Composition in Per Cent			
	Fe	Ni	Cu	Fe	Ni	Cu	Ag
Melt No. 25	25	25	50	20.6	18.3	1.5	59.6 (By Diff.)

The difference in iron and nickel percentages in the parent and displaced alloy is due to solution of these elements in the low-melting phase at the displacement temperature.

Iron-Lead and Iron-Magnesium

Specimens of 50-50 iron-lead were made by displacing the copper-rich phase with lead. When a sufficient head of lead was provided to last during a considerable cooling interval, it was found that exudation of lead continued, as the specimen cooled in the furnace, to about 700 degrees Fahr.

Iron-magnesium was made by displacing the copper-rich constituent directly with magnesium through the use of a nitrogen atmosphere and some pressure in the pipe container over the molten magnesium. It was later found that an intermediate step involving the displacement of the copper by lead and then the lead by such a material as magnesium avoids excessively high displacement temperatures.

Other low-melting metals which have little or no solubility for iron, such as Bi, Ba, Ca, or Sr, for example, could no doubt be employed as displacement constituents, but since no possible use for such alloys is known, trials were not thought worthwhile.

COPPER-BASE ALLOYS

In the iron-base alloys copper was employed as the low-melting element. A consideration of the copper-bismuth constitutional diagram indicated that copper could also serve as the high-melting or dendritic phase. Fig. 7.

A series of copper-base parent alloys containing from 10 to 90 per cent bismuth was made and displaced with lead for the purpose of establishing the composition limits for displacement. A bismuth content of 80 per cent caused the alloy to be so weak in the mushy stage that it fell through the holder, but the specimen with 70 per cent bismuth stood up (Fig. 8). The specimen containing 15 per

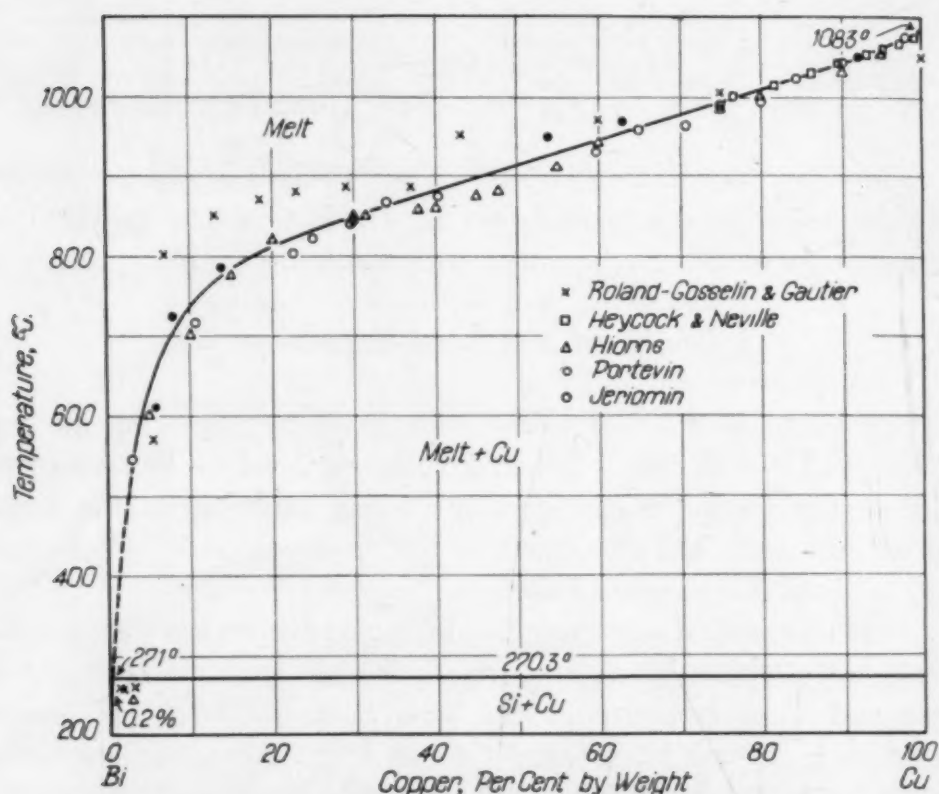


Fig. 7—Constitutional Diagram of the Copper-Bismuth System. Taken from "Der Aufbau der Zweistofflegierungen", p. 302, by M. Hansen.

cent bismuth and 85 per cent copper was completely displaced, although nitrogen pressure had to be used in order to effect a reasonably rapid flow of metal. The 10 per cent bismuth alloy could not be displaced.

Copper-Lead

In view of the fact that high lead, copper-lead alloys show an irregular distribution of lead, an effort was made to produce the material by displacement. In two displacements small percentages of silver and tin were added to the lead for their possible beneficial

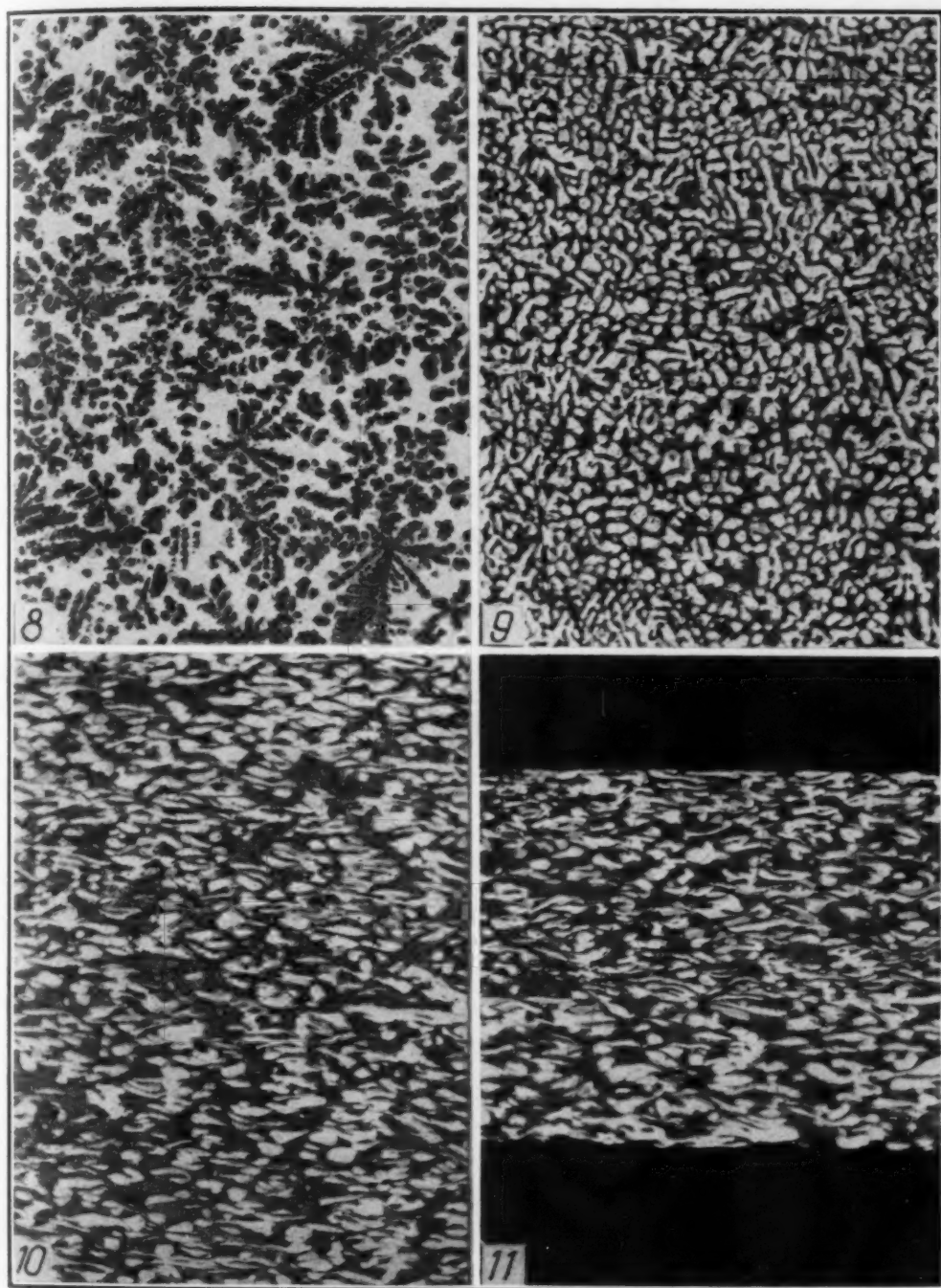


Fig. 8—Microstructure of a 70 Per Cent Bismuth, 30 Per Cent Copper Alloy. An $(\text{NH}_4)_2\text{S}$ Etch Has Darkened the Copper Dendrites. $\times 100$.

Fig. 9—Melt No. 182 Copper-Lead Alloy in the As-Displaced Condition. Unetched. $\times 100$.

Fig. 10—Sheet 0.050 Inch in Thickness Cold-Rolled from the Material Shown Above. $\times 100$.

Fig. 11—Sheet 0.015 Inch in Thickness Cold-Rolled from the Material Shown in Fig. 10. $\times 100$.

effects on resistance to lubrication corrosion. The following tabulation shows the results obtained as regards chemical composition.

Identification	Parent Alloy Calculated Analysis in Per Cent		Displacement Alloy Actual Analysis in Per Cent				
	Cu	Bi	Cu	Pb	Bi	Sn	Ag
Melt 181	50	50	47.1	52.2	0.02	<.05	<.05
Melt 182	50	50	47.0	52.2	0.04	<.05	<.05
Melt 184	55	45	51.9	45.7	0.05	<.05	1.33
Melt 186	55	45	52.7	46.6	0.03	<.1

Since copper and bismuth are miscible in all proportions above the liquidus, the distribution of copper and the low-melting bismuth-rich phase is quite uniform, subsequent displacements with lead gave the distribution shown in Fig. 9. It was found that displaced copper-lead alloys containing more than 40 per cent lead could be cold-rolled into thin sheet. Figs. 10 and 11 show microstructures of the sheet material.

Copper-Tin

Copper-tin alloys are, of course, readily made by conventional melting methods, but, with high-tin contents, the material is hard and brittle, on account of the presence of intermetallic compounds. Displacement of a copper-bismuth alloy was carried out with tin at 570 degrees Fahr. (300 degrees Cent.), and the specimen quickly quenched in order to reduce the time in which the molten tin and solid copper dendrites were in contact at elevated temperature. Subsequent microscopical examination and hardness tests showed that but little compound formation had occurred. Heating the specimen for 1 hour at 900 degrees Fahr. (480 degrees Cent.) caused rapid diffusion and a marked increase in hardness. Microstructures of these specimens are shown in Figs. 12 to 15, inclusive. Long etching makes it possible to recognize three structural constituents in Fig. 15; (a) remnants of almost pure copper dendrites, (b) zones next to the dendrites comparatively high in copper, (c) high tin zones in the interdendritic areas.

NICKEL-BASE ALLOYS

Fig. 16 shows the constitutional diagram of the nickel-bismuth system and Fig. 17 illustrates the microstructure of a 50 per cent nickel-50 per cent bismuth alloy. From about 30 to 80 per cent nickel, it can be seen by the constitutional diagram that there is a temper-

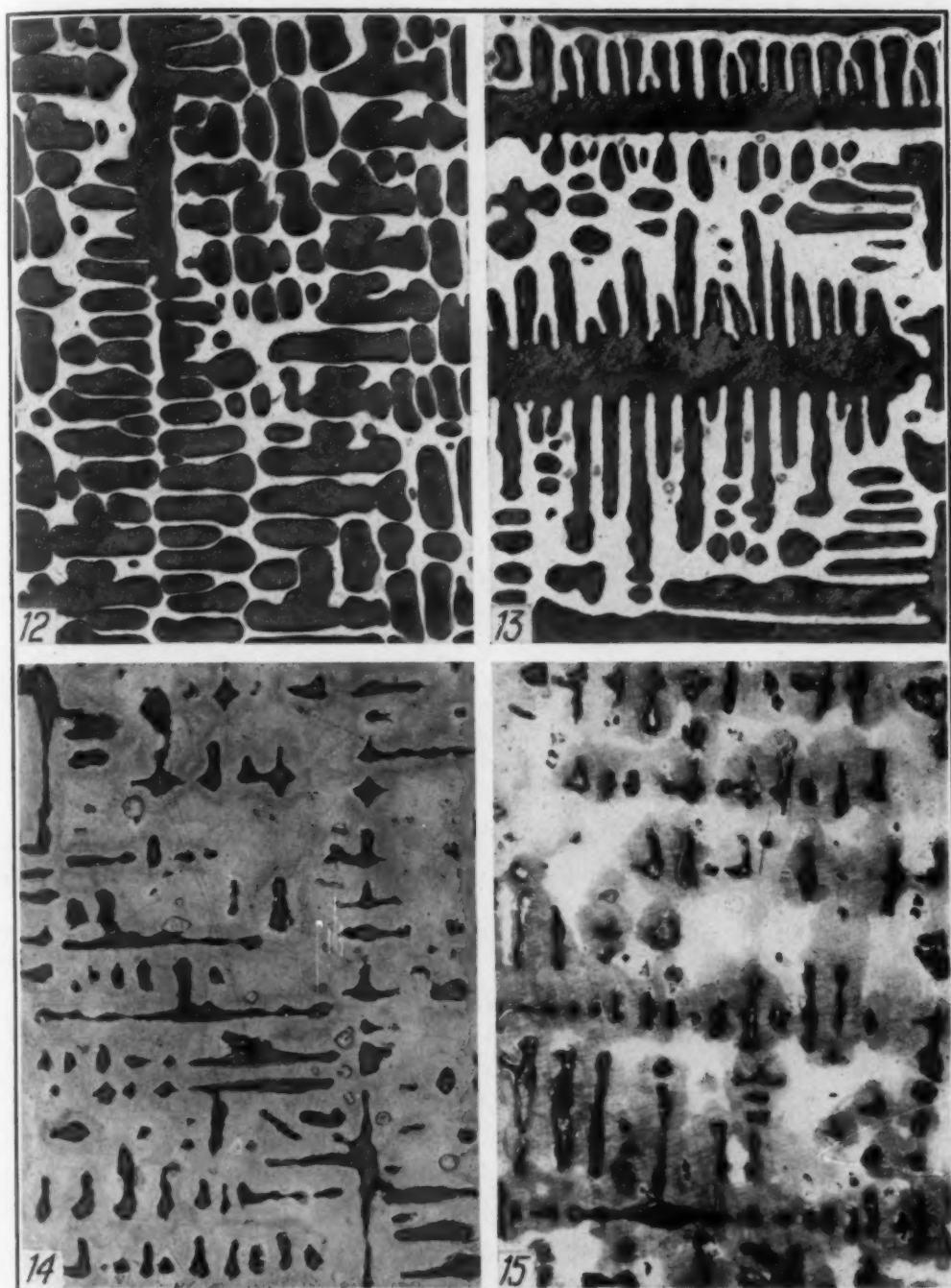


Fig. 12—Cu-Bi Alloy Slowly Cooled. The Copper Dendrites Have Been Darkened by the Etching Reagent While the Bismuth Filling Material was Unaffected.

Fig. 13—Structure After Displacing the Bismuth With Tin. Note that Very Little Alloying Action Between the Copper and Tin Has Occurred. "As Displaced" the Material Shows a Hardness—33 Rockwell B.

Fig. 14—Same as in Fig. 13 After Holding at 900 Degrees Fahr. for 1 Hour. Hardness—95 Rockwell B.

Fig. 15—Same as Fig. 14 After Much Longer Etching Time.

Photomicrographs of 100 Diameters Magnification. All Specimens Etched with $(\text{NH}_4)_2\text{S}$.

ature range of approximately 1110 degrees Fahr. (600 degrees Cent.), over which comparatively pure nickel dendrites exist in the low melting nickel-bismuth phase.

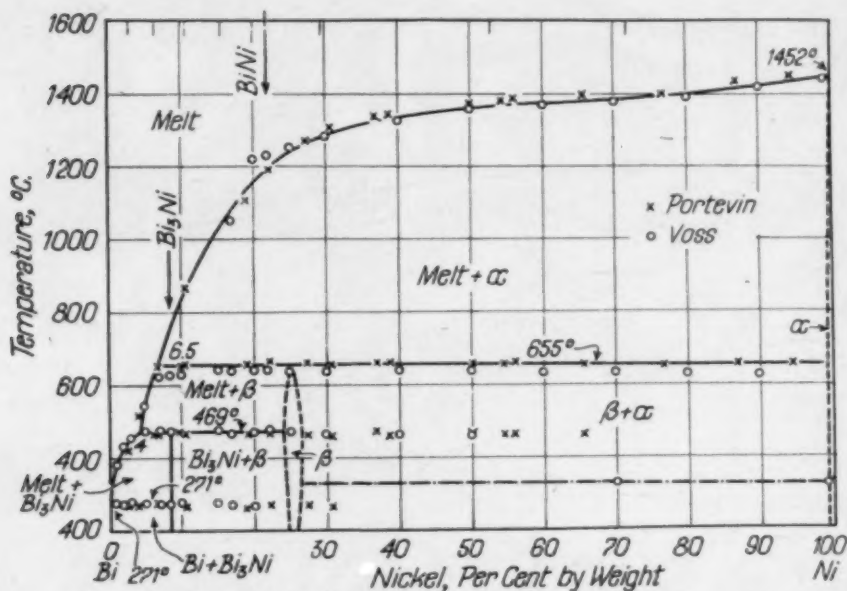


Fig. 16—Constitutional Diagram of the Nickel-Bismuth System by Portevin and Voss. Taken from "Der Aufbau der Zweistofflegierungen", p. 317, by M. Hansen.

Parent alloys of nickel-bismuth were made and displaced with silver at 1850 degrees Fahr. (1010 degrees Cent.). The completeness of displacement is shown by the following analysis:

Melt No.	Composition in Per Cent		
	Ni	Bi	Ag
54 (Ni-Bi) Parent Alloy	56.1	43.9	
54 (Ni-Ag) Displaced	43.3	0.04	55.3 (By Diff.)

In some cases it was found possible to roll the silver-nickel alloy into sheet and to draw it into wire. Figs. 18, 19, and 20 show the microstructure of the displaced alloy.

Some mechanical properties of the wire were determined after 77 per cent cold reduction and after annealing 3 minutes in a salt bath at 1200 degrees Fahr. (650 degrees Cent.).

Condition of Wire	Diameter, In.	Area, Sq. In.	Breaking Load, Pounds	Tensile Strength, Lbs./Sq. In.	Per Cent Elong.
(A) Drawn	0.062	0.00302	236	78,000	2.3
(B) Drawn	0.062	0.00302	260	86,000	2.3
(A) Annealed	0.062	0.00302	165	54,600	13.3
(B) Annealed	0.062	0.00302	183	60,600	13.3

The nickel-bismuth parent alloy is especially prone to develop

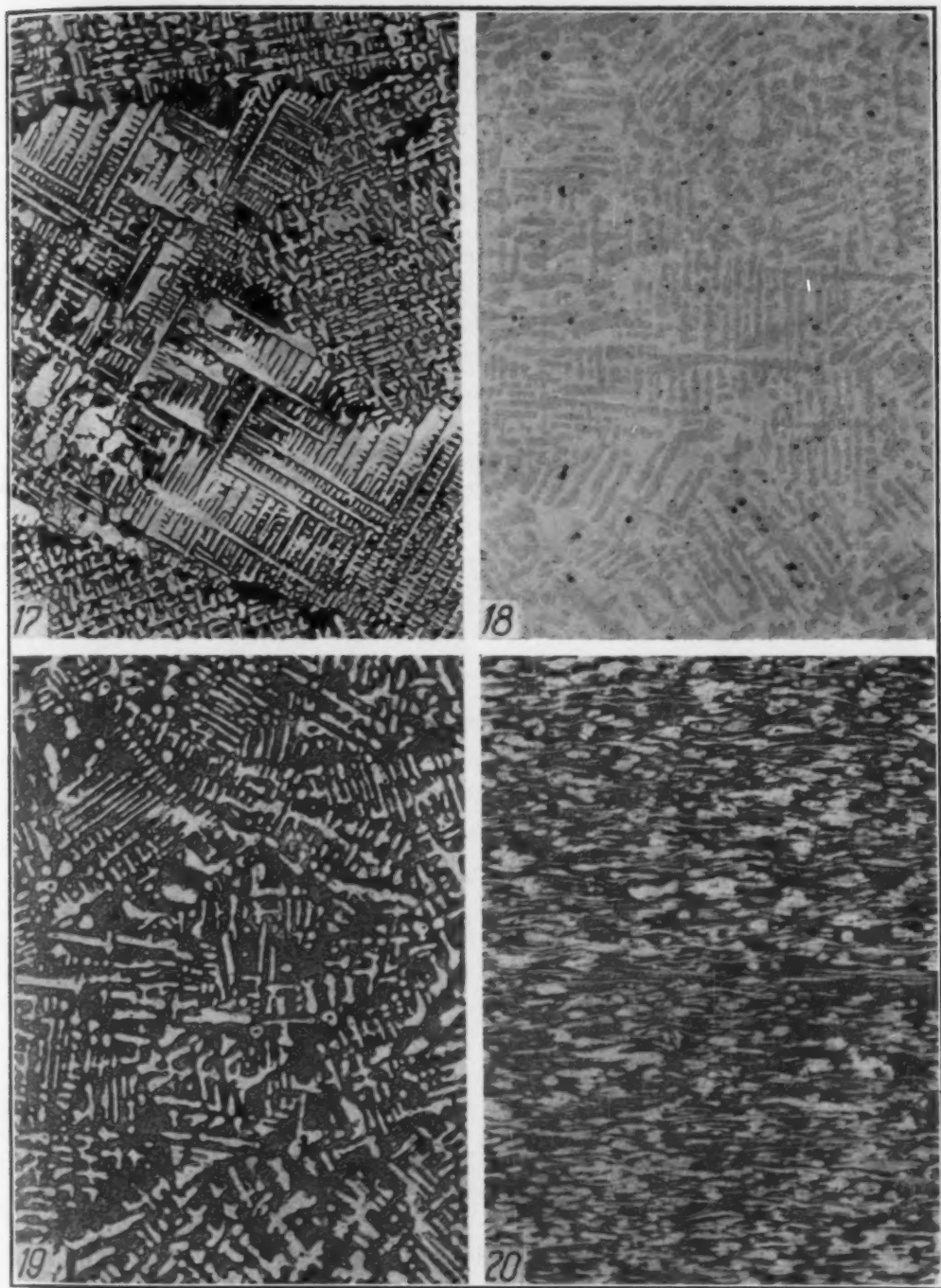


Fig. 17—Microstructure of a Nickel-Bismuth 50-50 Alloy After Etching in Acetic-Nitric Acid. Note that the Nickel Dendrites are White While the Bismuth-Rich Filling Material is Slightly Gray. $\times 100$.

Fig. 18—(Melt 206) Specimen of Silver-Nickel in the As-Displaced Condition. Unetched. $\times 100$.

Fig. 19—Same Specimens as Shown in Fig. 18 After Etching with Nitric-Acetic Acid. $\times 100$.

Fig. 20—Same as Fig. 19 After Rolling Into Sheet. $\times 100$.

interdendritic porosity and all of the voids are not completely filled with silver during displacement. It was found possible to forge and roll small specimens in some cases, but consistent results were never obtained because of porosity.

COBALT-SILVER ALLOY

Melts of cobalt-copper containing 60 per cent cobalt were made. In spite of the fact the constitutional diagram (Fig. 21) indicates that two liquids exist in the fully molten state, microscopical examination of the castings revealed no heterogeneity. The micro-

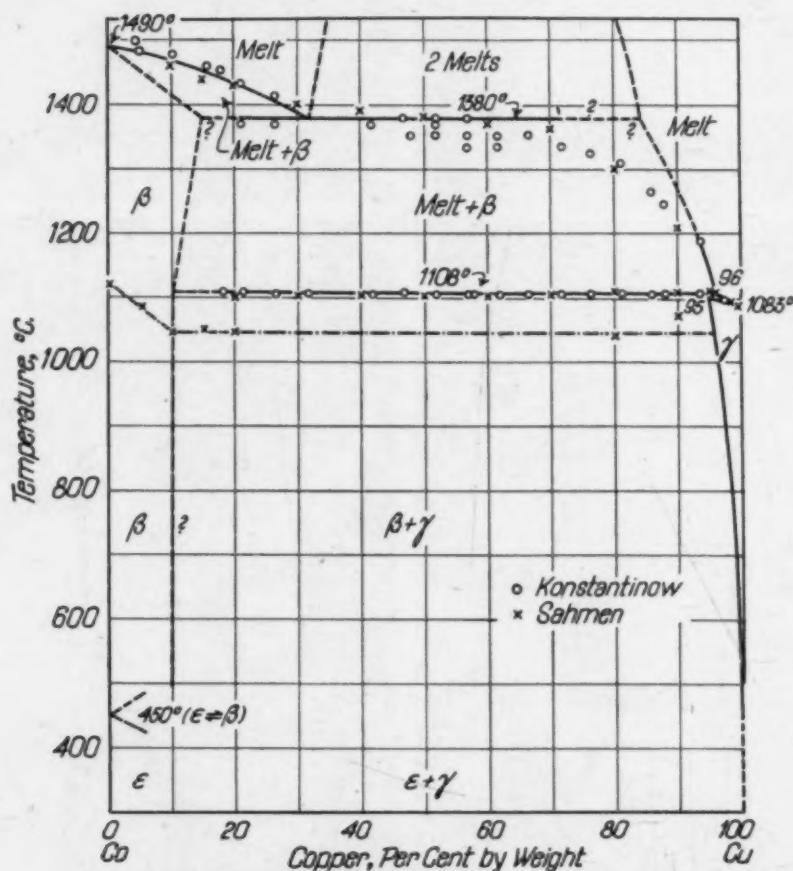


Fig. 21—Constitutional Diagram of the Cobalt-Copper System by Konstantinow and Sahmen. Taken from "Der Aufbau der Zweistofflegierungen", p. 484, by M. Hansen.

structure found was an exact duplication of that found in iron-copper alloys with cobalt-rich dendrites taking the place of the iron.

The cobalt-copper parent alloy was displaced with silver and the resulting cobalt-silver specimen drawn into wire. Figs. 23 and

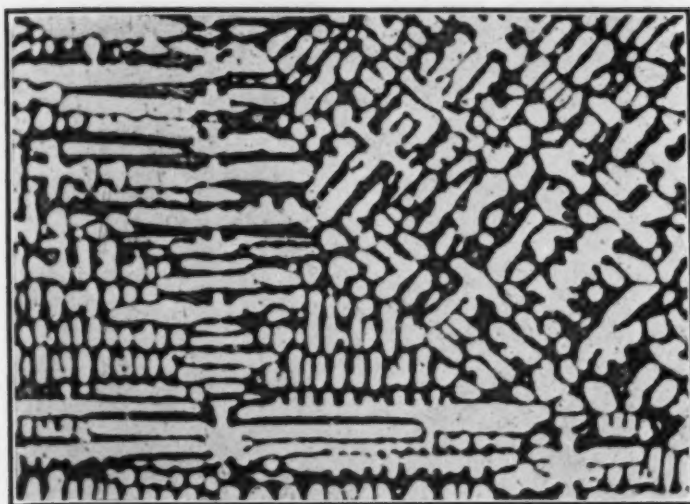


Fig. 22—Microstructure of a 60 Per Cent Cobalt, 40 Per Cent Copper Alloy After Heat Tinting. $\times 100$.

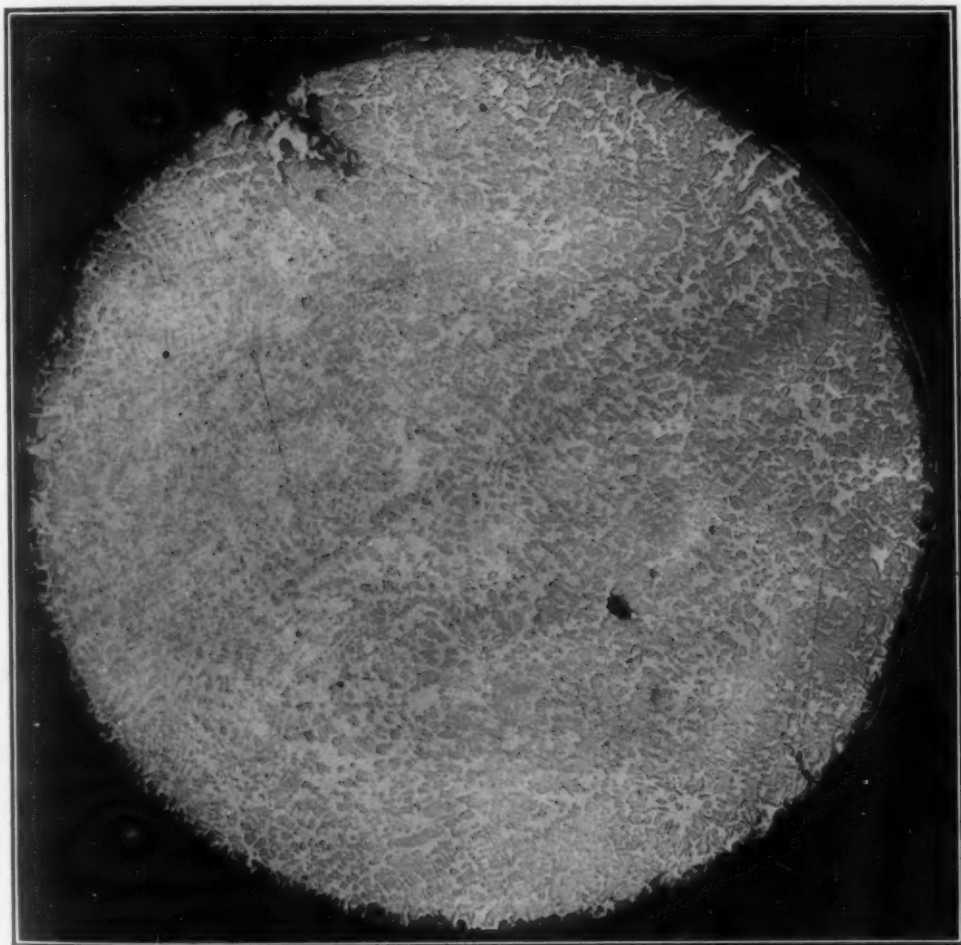


Fig. 23—Full Cross-Section View of a Cold-Drawn Wire Which Was Reduced from 0.370 Inch to 0.188 Inch in Diameter. Unetched. $\times 20$.

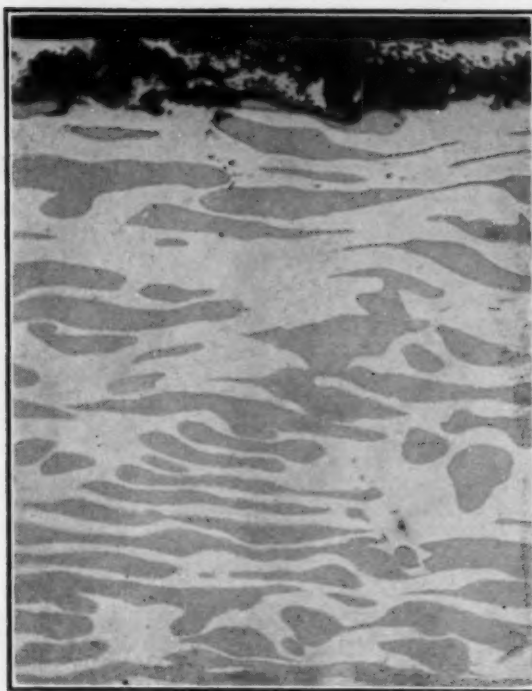


Fig. 24—Structure in a Longitudinal Direction at a Higher Magnification. The Darker Constituent is Cobalt. Unetched. $\times 100$.

24 show the microstructure of the wire. In this case the parent alloy was allowed to solidify in the furnace; hence, the particle size is large because of slow cooling.

ADDITIONAL ALLOYS PRODUCED BY DISPLACEMENT

A number of additional alloys have been made which do not merit detailed descriptions. The displacement alloys and the parent melts from which they were made may be listed as follows:

Displaced Alloy	Parent Alloy
Al-Pb	Al-Sn
Be-Mg	Be-Al
Ni-Pb	Ni-Bi
Co, Fe-Ag	Co, Fe-Cu
Co, Ni-Ag	Co, Ni-Cu

DEVELOPMENT OF A METHOD OF DIRECT DISPLACEMENT

In an effort to eliminate the cost of machining operations for both specimen and holder, attempts were made to carry out the dis-

placement operation directly in the crucible in which the parent melt was made. A hole was bored in the bottom of a clay-graphite crucible and fitted with a clay-graphite rod as shown in Fig. 25. A nickel-bismuth melt, covered by borax glass, was allowed to cool from 2650 degrees Fahr. (1455 degrees Cent.) to approximately 2050 degrees Fahr. (1120 degrees Cent.), and then molten silver was poured over the mushy parent alloy. Removal of the stopper rod permitted the

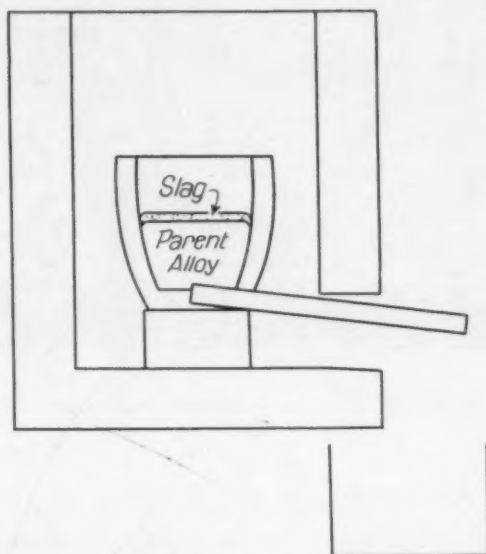


Fig. 25—Cross-Section Drawing of Crucible with Facilities for Side Tapping.

low-melting bismuth-rich liquid to exude from the bottom and, when practically pure silver came through, the rod was replaced in the hole. This method also eliminated interdendritic porosity from the nickel-bismuth material because the low-melting constituent was removed before it solidified.

The microstructure of a $\frac{1}{8}$ -inch sheet rolled from silver-nickel made directly is shown in Fig. 26. A serious disadvantage is that furnace cooling produced very large nickel dendrites and, hence, the particle size of the final alloy is quite large.

DISCUSSION OF RESULTS

Principles—The displacement method of producing certain alloys is in reality an indirect casting process. The high-melting or dendritic phase is cast as one constituent of an alloy from which it

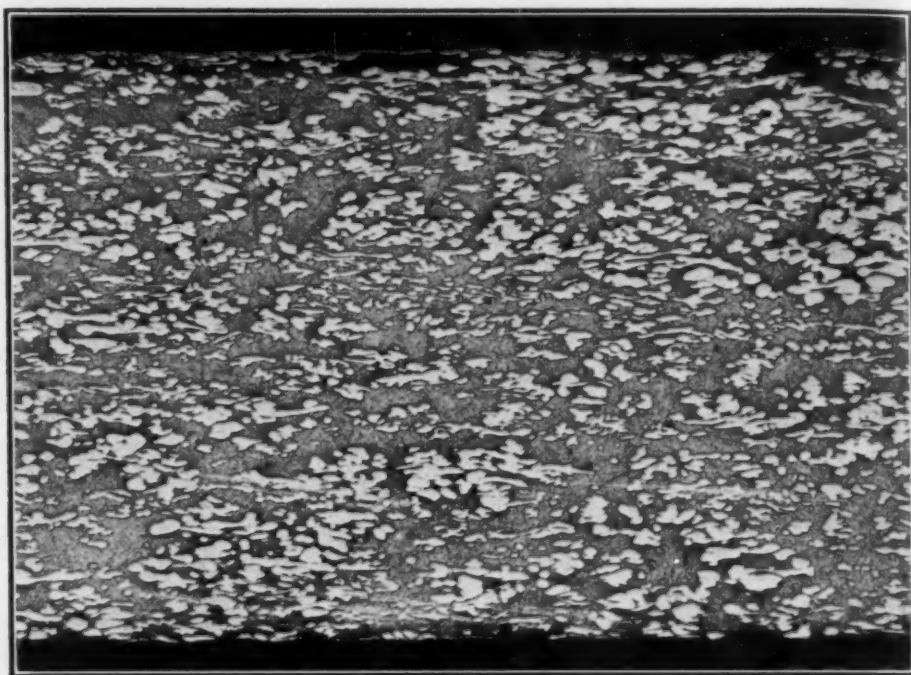


Fig. 26—Full Cross-Section View of a $\frac{1}{4}$ -Inch Silver-Nickel Sheet Rolled from Melt Displaced in the Crucible. Etched With Nitric-Acetic Acid. $\times 20$. Approximate Composition: Silver 60 Per Cent, Nickel 40 Per Cent.

separates during solidification in a uniformly dispersed condition, the size or distribution of the dendrites being controlled by the rate of freezing. The low-melting phase of this alloy is then displaced by another molten metal which assumes the same structural relationship to the high-melting component as did the original low-melting phase which was displaced, even though the new metal and the one composing the dendritic phase may have very little mutual solubility in the liquid state.

Molten aluminum and molten lead, for example, have little or no mutual solubility, and a liquid solution or chemical combination between the two metals cannot be obtained when the two melts are stirred together. The lead, having a specific gravity of approximately 11 as compared to 2.3 for aluminum, settles rapidly to the bottom of the mold, and, upon completion of solidification, two solid layers are found, the top layer being relatively pure aluminum and the bottom relatively pure lead.

Aluminum and tin, however, are completely soluble in the liquid state and only slightly soluble in the solid state. Fig. 27. Upon cooling from the fully molten condition, dendrites of practically pure aluminum grow throughout the melt with the tin remaining liquid and

constituting the interdendritic constituent. No separation or liquation occurs because the dendrites are growing *from* the melt and a high degree of uniformity as regards the distribution of the two phases is found upon complete solidification.

When the aluminum-tin alloy is reheated to a temperature at which the tin-rich liquid is molten, but at which the aluminum dendrites are still solid, and molten lead caused to displace the tin-rich liquid, a homogeneous aluminum-lead alloy is obtained having exactly

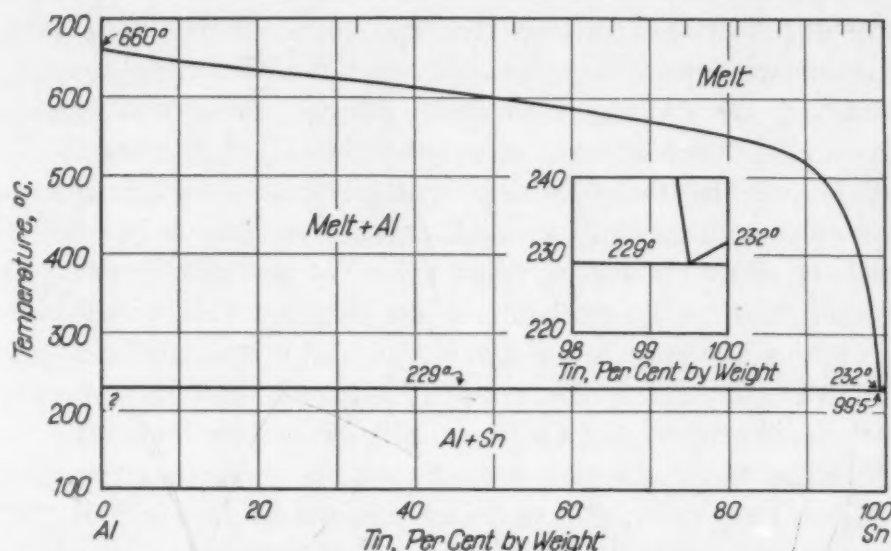


Fig. 27—Constitutional Diagram of the Aluminum-Tin System by Roland-Gosselin. Taken from "Der Aufbau der Zweistofflegierungen", p. 153, by M. Hansen.

the same structural relationship as did the original aluminum-tin alloy. The same reasoning applies to other metallic systems, such as the iron-silver, nickel-silver, and iron-lead combinations. Some possible practical applications of the displacement method for making certain alloys are given in U. S. Patent No. 2,209,935 which was issued in 1940.

It has been found that to displace completely parent alloys, consisting of about 20 per cent low melting phase and 80 per cent dendrites, it is necessary to put through the parent specimens an amount of displacing metal equal to the weight of the specimen. Complete displacement of parent alloys containing 50 per cent high melting phase or dendrites and 50 per cent of the low melting constituent requires about twice the weight of the specimen.

Some affinity between the dendrites and the displacing liquid can be countenanced, provided the melting point of the displacing

metal is far lower than that of the dendritic phase, and that the time of contact at elevated temperatures is not too long. The copper-tin alloy shown in Fig. 13, for example, was quenched 80 seconds after the molten tin was first in contact with the copper; hence, little or no intermetallic compound formation occurred.

The removal of the original low-melting liquid and the entrance of the displacing metal seem to be intimately related. In attempting to prepare a catalyst material in the form of a dendritic sponge, it was found impossible to remove the filling metal completely by forcing dry hydrogen through the specimen. After a passageway for the gas was opened up through some exudation, higher pressure only caused the hydrogen to rush through these openings more rapidly and did not effect a complete removal of the interdendritic liquid. Once the interdendritic channels are opened, as through displacement with mercury and subsequent evaporation in a hydrogen atmosphere, they cannot be filled again by a molten metal. This phenomenon offers an explanation for the fact that nickel-bismuth parent alloys showing interdendritic porosity resulted in a porous nickel-silver alloy after displacement, whereas perfectly sound original or parent alloys produced a sound nickel-silver material.

Relation of the Displacement Process to Inverse Segregation— In addition to considerable practical significance, the subject of inverse segregation has attracted the attention of many investigators simply from the viewpoint of academic interest. The hypotheses for explaining the mechanism by which the low-melting constituent reaches the location where it would be least expected have been divided into two classes. In one group the assumption is made that something happens to the melt which causes crystals of the low melting phase actually to solidify first, hence, they occur on the chill face of the casting. In the second group the supposition is that solidification starts in a perfectly normal manner but that the low-melting liquid migrates from the center to the surface prior to complete solidification. A number of forces have been suggested as the cause of migration of the liquid but there is no general agreement as to their relative importance in any particular case.

The first group of hypotheses arose mainly from studies of salt solutions and of other systems differing radically from metals. These hypotheses can be dismissed as having at least a very minor effect from the metallurgical viewpoint.

In the class of hypotheses which postulate that freezing starts

with normal micro- or dendritic segregation but that, subsequently, a migration of the low-melting phase occurs, some are almost as fantastic as those in the first group. Watson's (9) theory that primary crystals form on the mold wall and then migrate toward the center of the casting was not substantiated by experimental evidence. Concurrence with the crystallization pressure theory of Masing and Haase (8), which supposes that the inward growing dendrites exert a pressure on the liquid in the interior and expel it toward the outside requires at least a credulous attitude. The contraction pressure theory proposed by Kühnel (5) postulates the formation of a crystalline envelope surrounding the molten metal and the subsequent contraction of the solidified shell away from the mold wall. Hydrostatic pressure of the liquid interior is said to increase until the envelope bursts and the low melting liquid flows through the cracks, filling the space between the original shell and the mold. This theory apparently does not take into account the fact that the liquid interior is shrinking too because of falling temperature and progressive solidification on its outer shoreline.

Genders (7) believes that gas evolution during the latter stages of solidification is the primary cause of all inverse segregation. The solubility of various gases becomes less as the temperature falls and especially upon solidification. Gas liberated during the mushy stage is thought to expel the liquid through the interdendritic channels to the outside surface. Other investigators—Gayler (11), Böhner (12), Fraenkel and Godecke (13)—have questioned Genders' hypothesis and, among other things, cited experimental evidence showing that inverse segregation had been observed in castings made from melts produced in vacuum in which, of course, the gas content would be quite low.

The interdendritic flow theory proposed by Bauer and Arndt (6) for explaining inverse segregation seems to be the most reasonable explanation. Genders' theory of gas evolution can no doubt play an important part in supplying the force necessary to cause the liquid to flow through the minute channels, acting in this respect much like the nitrogen pressure used in displacement to speed up the exudation. Gravity alone can be sufficient in many cases to cause the flow, and the interdendritic voids, so often found in the interior of castings showing inverse segregation, may be a result of the flow of the low melting liquid rather than the cause of exudation through gas evolution as generally supposed.



Fig. 28—Dendritic Pattern Developed by Etching a 1.4 Per Cent Silicon, Copper-Silicon Alloy. $\times 3$. (Photograph by J. C. Fisher).

The original or parent alloys used in the experiments described above, iron-copper, cobalt-copper, beryllium-aluminum, copper-bismuth, nickel-bismuth, aluminum-tin, for example, show comparatively low solubility of the two metals in the solid state and, also, a long solidification range or mushy stage. It was possible, therefore, to hold them at a temperature interval within the mushy stage indefinitely, without closing the interdendritic channels, so that interdendritic flow could take place.

During the freezing of alloys which exhibit unlimited solubility in the solid state, within the composition range covered, the primary crystals (dendrites) rich in the high-melting metal form first. The interdendritic liquid is rich in the low-melting phase, but, under equilibrium conditions, diffusion from the liquid to the solid occurs. If cooling is rapid, diffusion is incomplete and the casting may contain well-defined dendrites, as shown in Fig. 28.

The conditions existing for a short time interval during the

freezing of an alloy similar to the one shown in Fig. 28 must be very similar to those attending the freezing of the parent alloys listed above. The first shell formed on the mold surface consists of skeleton crystals surrounded by continuous interdendritic channels through which flow can occur, provided there is an outer space into which the liquid can go and sufficient pressure or urge to cause the movement.

Ordinarily, diffusion and falling temperature shut off the channels, but in the case of nonferrous alloys showing a long solidification interval, such as aluminum-copper, copper-tin-lead, and phosphor bronze, the low-melting liquid may flow through the interdendritic channels and collect as "sweat" on the outside surface. A more serious consequence than the mere loss of an element, intentionally added for a definite purpose, is incipient or interdendritic porosity developed in the interior of the casting, which adversely affects the mechanical properties.

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DISCUSSION

Written Discussion: By L. R. vanWert, chief, Metallurgical Division, Research, Leeds and Northrup Co., Philadelphia.

This is a very interesting paper, and the authors are to be congratulated for the contribution it makes to our knowledge of what can, and in the cases cited does, happen when two dilute solid solutions freeze consecutively, but at widely separated temperatures, from a melt. Inverse segregation is a fascinating solidification phenomenon that has called forth a great deal of speculative thought. But the phenomenon has important and far-reaching practical implications, and I welcome this report as much for the ingenious way the authors have made workable alloys whose constituents are immiscible in the solid state as for their convincing demonstration of the validity of the interdendritic flow theory as an explanation of the phenomenon.

Written Discussion: By J. C. McDonald, The Dow Chemical Co., Midland, Mich.

The authors mention the fact that they have made alloys of beryllium and magnesium, and describe briefly the process by which they made alloys of iron and magnesium. Could they tell us something about the structure and properties of these alloys?

A number of people have endeavored to alloy beryllium with magnesium, without much success. Because of the low density of high beryllium-magnesium alloys, and the probably high modulus, knowledge of other properties of these alloys would be most interesting.

Alloys of iron and magnesium are of interest for one reason because of their usefulness in studying the corrosion of magnesium. It has been established that this corrosion is largely electrolytic in nature, with particles of iron as the chief source for the electrolytic couples. By producing alloys sufficiently low in iron, this cell action is nearly completely eliminated. But by having alloys high in iron, it becomes much easier to study the fundamental nature of what goes on at these cells.

The authors state that at one time they exposed molten magnesium to an atmosphere of N_2 . I would like to point out that under certain conditions magnesium will burn in an N_2 atmosphere. Such exposure cannot be recommended as good practice. There are only a few atmospheres to which magnesium is completely inert, the chief of which are helium and hydrogen.

Written Discussion: By Cyril Stanley Smith, research supervisor, War Metallurgy Committee, Washington, D. C.

This paper is of considerable interest, not only because of the proposed new

method of making certain alloys, but also because the paper suggests a new method for studying the composition of the solid phase in alloys in the semi-liquid condition. In the past, some studies have been made by removing a few solid crystals from the molten metal in which they are in equilibrium. The authors' method of removing the melt from the solid phase seems to offer some advantages.

The authors' analyses of their iron-silver alloy, that had been made by replacing the copper-rich phase in an iron-copper alloy with silver, show only 2.7 per cent of copper. On the basis of a silver-free alloy this is equivalent to 5.7 per cent copper, which is supposedly the composition of the iron-rich phase formed during solidification of the initial iron-copper alloy. This is considerably less than would result if the dotted line LI in the constitution diagram (Fig. 5) were correctly placed. Likewise, the iron-rich phase in the iron-nickel-copper alloy, after replacing with silver, contains 1.5 per cent copper, or 3.7 per cent on a silver-free basis. This would indicate that copper is actually less soluble in the iron-nickel alloy than in iron itself.

Such figures at best are approximate, since it is unlikely that equilibrium existed in the original casting and it is possible that some copper may have been removed by diffusion and solution in the liquid silver. On the whole, however, it seems that the authors' method with a little refinement would prove to be a very useful tool for the study of alloys in the semi-liquid condition. With proper temperature control the displacement technique could be applied even to alloys in which the solidification range is much narrower than the examples chosen. I expect it to prove valuable in the study of solidification mechanisms.

Does the relative surface tension of the displaced and displacing metals affect the completeness of replacement in any degree? Do the authors care to enlarge on the advantages of their method of preparing immiscible alloys compared with the well-established methods of powder metallurgy?

Oral Discussion

F. N. RHINES:¹ I simply wish to congratulate the authors most heartily on this ingenious study. It appears to have established, beyond reasonable doubt, the basic mechanism of inverse segregation, which has so long been a subject of controversy. The unusual coincidence of an important scientific finding and a new technique for accomplishing a practical result, in a single piece of research is noteworthy indeed upon the basis of rarity alone.

Authors' Reply

We appreciate the generous comments made on this paper. The investigation started as a study of the mechanism involved in inverse segregation and the finding of a circuitous method for producing a number of unusual alloys was a subsequent development. There is naturally a great deal which is not known about the subject but the authors will attempt to answer questions raised in the discussion.

¹Assistant professor, department of metallurgy, Carnegie Institute of Technology, Pittsburgh.

In answer to Mr. McDonald's question concerning the properties of iron-magnesium and beryllium-magnesium alloys, we made only one small specimen of each of these alloys (about 50-50 composition) to determine whether they could be made; consequently, no mechanical tests were run.

Mr. McDonald is correct in saying that it is not good practice to expose molten magnesium to an atmosphere of nitrogen. It is mentioned in the paper that rather than to carry out the displacement of copper with magnesium at a temperature above the melting point of copper, an intermediate step be used which consists of first displacing the copper with lead and then at a much lower temperature displacing the lead with magnesium.

No unqualified explanations can be suggested for the lack of agreement between the amount of residual copper obtained after displacement of the copper-iron alloys and that shown tentatively by the equilibrium diagram other than those mentioned by Dr. Smith. Even the absence of equilibrium conditions in the solidification of the original iron-copper alloy may not have much influence in this particular case because of the nearly vertical position of the solidus line IL. The composition of the solid solution formed during freezing does not change appreciably with the composition of the melt but remains, according to the diagram, close to 7.5 per cent copper. As the composition of the melt changes along BCDE, a solution of the composition IL continues to form until that of the melt reaches E. At this point solidification is completed by the formation of a copper-rich solid solution of the composition M. Hence, fast cooling of the original melt should not produce primary crystals with cores poor in the low melting constituent as is the case during the freezing of most solid solutions. The unusual nature of this portion of the copper-iron equilibrium diagram naturally raises a doubt as to the proper location of the solidus line IL.

The possibility that some of the copper dissolved within the dendrites may be removed by diffusion into the molten silver which passes through the interdendritic channels will have to be checked by careful chemical analysis at different stages in the displacement operation. The use of displacing metal which has no appreciable solubility for either the high melting dendrites or the element in solution would eliminate this possible source of error. However, the results of tests in which attempts were made to displace the bismuth-rich phase of a copper-bismuth parent alloy with grease or with various salts indicate that the metal being displaced should be somewhat soluble in the displacing liquid or displacement will not be complete.

The lower percentage of copper within dendrites consisting of a solid solution of nickel in iron is not what one would expect but is not an unusual metallurgical phenomenon. Relatively pure iron, for example, can hold about 2.8 per cent phosphorus in solution at room temperature but in the presence of carbon, silicon, and other impurities, iron phosphide eutectic may be observed with less than 0.50 per cent phosphorus even in massive sections. Another possible explanation for the iron-nickel solid solution being lower in copper than pure iron is that the rate of diffusion of copper through the solid solution may be much higher than in relatively pure iron with the result that more copper would be removed from the solid solution.

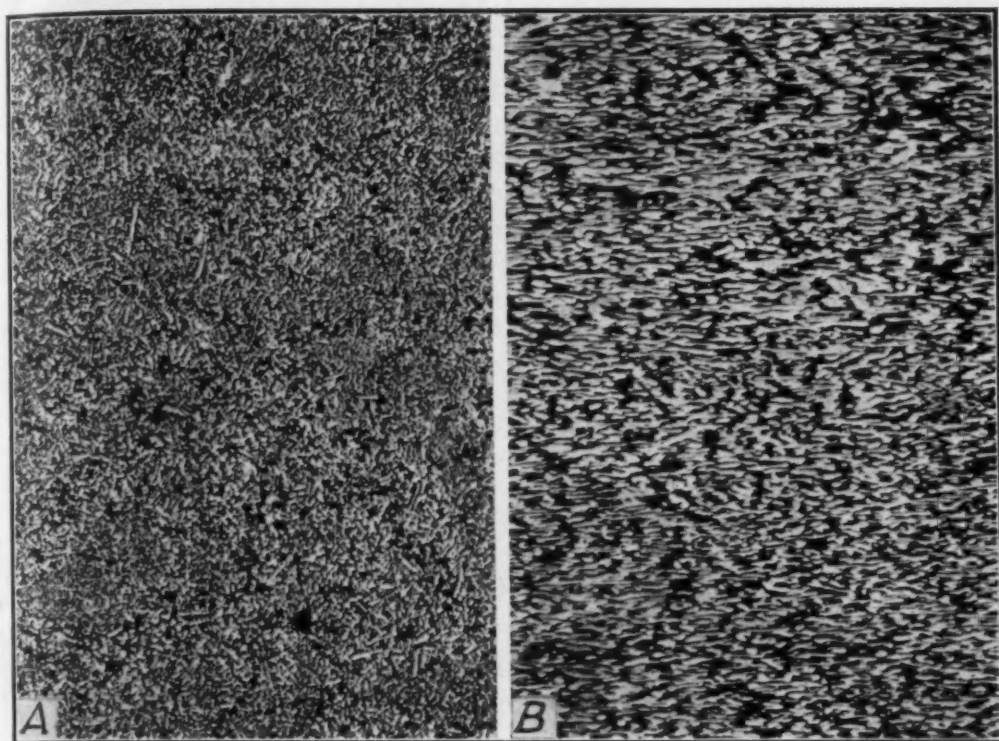


Fig. A—Cross-section of Silver-Nickel Wire After Etching with Ammonium Sulphide. The Silver Has Been Blackened with a Coating of Silver Sulphide. $\times 20$.
Fig. B—Longitudinal Section of the Specimen Shown in Fig. A. $\times 20$.

We think that Dr. Smith's suggestion that chemical analysis of some displaced alloys might be useful in showing the limits of solid solubility is well worth following up with experiments planned for that purpose. It may be noted in Fig. 7 that the equilibrium diagram for the copper-bismuth system indicates no solubility of bismuth in copper. The displaced alloys ranged in bismuth content from 0.05 to 0.02 per cent. In view of the fact that the lead employed for displacement probably contained a small amount of bismuth, it seems that there is rather good agreement between these results and the diagram. A number of binary constitutional diagrams show a long solidification interval and only tentative boundaries as to solid solubility. The following could probably be studied by means of this method:

- | | |
|--|--|
| 1. Solubility of beryllium in silver | 8. Solubility of mercury in lead |
| 2. Solubility of bismuth in silver | 9. Solubility of mercury in zinc |
| 3. Solubility of lead in silver | 10. Solubility of bismuth in nickel |
| 4. Solubility of thallium in silver | 11. Solubility of antimony in chromium |
| 5. Solubility of silver in silicon | 12. Solubility of copper in iron |
| 6. Solubility of aluminum in beryllium | 13. Solubility of antimony in iron |
| 7. Solubility of mercury in aluminum | 14. Solubility of zinc in magnesium |

It is not known to what extent the relative surface tension of displaced and displacing metals determines the success of the operation. It was found

impossible, however, to completely displace alloys containing either sulphur or phosphorus as a low melting constituent. Both nickel-sulphur and nickel-phosphorus appear suitable from the diagrams and did produce parent alloys consisting of nickel dendrites in low melting matrices. Silver or lead was passed through the specimens which caused some exudation of the eutectic material but displacement was never complete. The difference between the action of true metals and these metalloids was thought to be related to surface tension or to the insolubility of the displacing liquid and the metalloids.

There are possibly two advantages of the displacement method over powder metallurgical methods. First, much larger section sizes could be produced because of pressure difficulties in the powder method. This assumption is based upon the fact that a 12-pound specimen of iron-silver was made just as easily as specimens weighing only a few hundred grams. Presumably, specimens weighing several hundred pounds could be handled without great difficulty. Second, a more uniform distribution of structural constituents in the displaced material may be obtained under proper conditions. Figs. A and B illustrate a rather uniform distribution of silver and nickel in a specimen of the displaced material.

A serious disadvantage of the displacement method, of course, arises from the necessity of refining the exuded material. This product consists of varying percentages of both high and low melting constituents in the parent alloy as well as the displacing metal.

THE ALPHA IRON LATTICE PARAMETER AS AFFECTED BY MOLYBDENUM, AND AN INTRODUCTION TO THE PROBLEM OF THE PARTITION OF MOLYBDENUM IN STEEL

BY FRED E. BOWMAN, ROBERT M. PARKE, AND ALVIN J. HERZIG

Abstract

Methods of determining quantitatively the partition of molybdenum between cementite and ferrite in steel are discussed. It is concluded that measurement of the lattice parameter of alpha iron solid solutions of molybdenum is the most promising means of securing the required partition data.

The relation between the alpha iron lattice parameter and the molybdenum content has been determined for binary iron-molybdenum alloys by means of X-rays and will be used to measure the distribution of molybdenum between ferrite and carbide in the iron-rich ternary iron-carbon-molybdenum alloys.

DESPITE the wide application of alloy steels and cast irons, resulting from their highly useful properties, very little can actually be said relative to the physical principles underlying the benefits produced by alloys. The ability, for instance, of small amounts of molybdenum to influence, to a remarkable degree, the hardenability of steel is recognized, but any attempt at an explanation fails, owing to the lack of sufficient fundamental information. The need for knowledge concerning the location of the atoms of added elements in the austenite transformation products frequently arises in discussing the effects of these added elements on the physical properties of steel. It is characteristic of most of the alloying elements to segregate in either the ferrite or carbide phase. Molybdenum has been regarded as being in that class of elements that concentrate in the cementite, but quantitative data are lacking. Furthermore, it would add much to our understanding of the heat treating processes applied to molybdenum steels and cast irons to

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. The authors are associated with the research laboratory, Climax Molybdenum Company, Detroit. Manuscript received June 29, 1942.

know the effect of carbon content, molybdenum content, and temperature of austenite transformation on the partition of molybdenum between ferrite and cementite. For this reason an investigation of the distribution of molybdenum between the ferrite and carbide phases in steel, to which this paper is an introduction, has been undertaken.

Although it is impossible at present to find any definite relation between the physical characteristics of molybdenum-bearing steels and the partition of molybdenum, several possible connections can be pointed out. It has been established that the presence of molybdenum retards the rate of austenite transformation at temperatures above 900 degrees Fahr. (480 degrees Cent.), that is, in the region where transformation is certainly a process of nucleation and growth. The reasons for the changes in the decomposition reaction rates are obscure at present; but, if it can be shown that the molybdenum concentration of the carbide is governed by some definite natural law, the mechanics of the delay becomes more apparent. The necessity for diffusion of a third element, a process generally much slower than the diffusion of carbon, would aid in accounting for the lag in nuclei formation as well as the decrease in rate of growth.

Other phenomena that may be related to the distribution of molybdenum in steel and cast iron are the rate of softening of martensite and the effect of molybdenum upon graphitization of the carbide.

PREVIOUS WORK ON THE PROBLEM

To the early workers in the field of molybdenum steels, the distribution of molybdenum between ferrite and carbide proved to be of more or less academic interest. It was known that molybdenum readily formed a carbide, and its presence in cementite was anticipated. The existence of a double carbide with iron was established early in the study, by Guillet (1),* from microscopic examination, and later identified as a nonmagnetic constituent in the residue from chemical separations, by Swinden (2), and Arnold and Read (3). It was conclusively differentiated from cementite when the crystal structure was established by Westgren and Phragmen (4). Because of the fineness of this double carbide when present in low

*The figures appearing in parentheses pertain to the bibliography appended to this paper.

concentrations, it is difficult to fix accurately the lower composition limit of this phase. Nevertheless, it seems safe to say that it is not formed in steels containing less than 1 per cent molybdenum, regardless of carbon content.

On a tonnage basis, by far the largest portion of molybdenum-bearing steels contain less than 1 per cent of this element, yet practically all the work pertaining to the partition problem has been conducted on materials having 1 per cent as the lowest molybdenum concentration. Since it is intended to confine the present work to alloys of low molybdenum content, it would be unprofitable to cite in detail the results of these earlier investigations. However, to exemplify the confusion existing in the state of the knowledge, the conclusions reached by several of these workers will be examined. On the basis of measurements of electrical resistance Portevin (5) concluded that molybdenum up to 5 per cent was dissolved wholly in the ferrite; but, from results obtained by similar means Swinden (6) decided that in annealed steels no molybdenum existed in solid solution. Gregg (7) quotes an unpublished report by Lester as concluding from microscopic and X-ray data that molybdenum up to 2 per cent tends to go into solution in the ferrite. Takei (8) made a magnetic study of the ferromagnetic carbides in molybdenum steels and postulated from his results that cementite is capable of dissolving both molybdenum and iron. The results of preliminary work carried out in this laboratory (9) show definitely that the molybdenum content of the carbide is appreciably greater than that of the parent austenite.

SELECTION OF THE METHOD TO BE EMPLOYED IN THE PRESENT WORK

In considering the possible methods available for determining the distribution of molybdenum, those employed in the previously mentioned investigations were given serious thought. The determination of the molybdenum content of the ferrite by measurement of the electrical resistance of the alloy necessitates the assumption that the carbide exerts no effect. It is felt that this assumption is unsound, since it seems unreasonable to suppose that the carbide in lamellar pearlite offers no more restriction to current flow than when in the spheroidized condition. If, as is necessary, the carbide is assumed to be a nonconductor, the plates of this material lying normal to the direction of current flow would effectively block its path and

decrease the cross sectional area of the ferritic conducting medium.

An application of a magnetic analysis to the partition problem involves the determination of changes in the Curie point of the carbide (8) or ferrite, or the change in intensity of magnetization of the ferrite produced by dissolved molybdenum (10). The latter property is too slightly affected by molybdenum contents in the range to be considered in the present problem. Since the Curie transformation of cementite occurs over a range of temperature, there is no definite value that may be correlated to variations of composition.

Chemical separation and subsequent analysis of the carbides seems, on the face of it, to be the most direct method of obtaining the desired information. In the course of the work previously mentioned (9), however, several serious difficulties were encountered. The method was found to work satisfactorily for coarse spheroidized and lamellar carbide structures, but failed completely when used for the finer structures resulting from transformation of austenite below 1200 degrees Fahr. (650 degrees Cent.).

The rapid advancement made during recent years in the application of X-ray diffraction methods to constitution-diagram work suggested its use in this problem. The sensitivity of the solid solution lattice parameter to changes in composition affords a convenient method for determining composition, once the relationship is known. By the use of the back-reflection camera, which utilizes the reflections from planes of relatively high indices, it is possible to determine the lattice constant with high accuracy. Furthermore, from the work of Burns (11), it does not appear that carbon, in the minute amounts that are soluble in ferrite at room temperatures, will significantly change the lattice parameter of alpha iron. For these reasons it was decided that the measurement of the ferrite and, if possible, the carbide lattice parameters by means of the back-reflection camera presented the most promising method of obtaining partition data.

DETERMINATION OF THE RELATIONSHIP BETWEEN MOLYBDENUM CONTENT AND LATTICE PARAMETER

In order that the method be applicable to the iron-carbon-molybdenum alloys, it is necessary to know precisely the relationship between the ferrite lattice parameter and the molybdenum content. X-ray data on the iron-molybdenum alloys reported by Chartkoff

and Sykes (12) reveal only that at saturation, about 22 per cent molybdenum, the iron lattice is expanded 1.3 per cent. Obviously, these data are not in the range desired.

The partition is to be investigated eventually in iron-carbon-molybdenum alloys containing less than 1 per cent molybdenum; therefore the molybdenum content of the binary alloys was varied from zero to about 1 per cent.

Preparation of the samples, a matter of utmost importance in work of this type, was carried out with extreme care. Electrolytic iron and pure molybdenum (hydrogen reduced) in approximately 500-gram charges were melted in magnesia crucibles, under vacuum, in an Ajax high frequency furnace. At no time during the melting process did the pressure exceed 3 millimeters of mercury, and this maximum was attained for only a short time during actual fusion. The charge, after being held molten for 10 minutes under a pressure of less than 1 millimeter, was allowed to solidify in the crucible. No evidence of crucible attack was noted. The ingots were forged to $\frac{1}{4}$ -inch square bars. After removal of forging scale, the bars were annealed in a vacuum of less than 10 microns (0.01 millimeter) of mercury. One hundred hours at 2250 degrees Fahr. (1230 degrees Cent.) was found necessary to produce an alloy sufficiently homogeneous to yield sharp diffraction patterns. The alloys were always cooled slowly to room temperature to avoid any possibility of supersaturating the ferrite with respect to carbon, since it is possible, by quenching from just below the A_{e1} , to retain in solution sufficient carbon to expand the ferrite lattice materially (11). A typical analysis follows:

	Per Cent
Carbon	0.006
Manganese	0.001
Silicon	Less than 0.001
Sulphur	0.006
Nickel	Less than 0.001
Chromium	Less than 0.001
Lead	Less than 0.001
Insoluble	0.008

Lead is reported because certain electrolytic irons have been found to contain appreciable quantities of this element, apparently traceable to the "insoluble" anodes employed in the electroplating process.

The diffraction cameras employed were of the back-reflection focusing type, as described by Mikulas, Thomassen, and Upthegrove

(13). Unfiltered radiation from a Siegbahn-Hadding gas tube with a cobalt target was used. Exposure times ranged from 30 to 40 milliampere-hours.

The measurements taken between corresponding lines on the film are related to Θ , the Bragg angle, by the following

$$\Theta = 90 - \frac{22.5 L}{\pi R},$$

where L is the distance between the lines and R is the camera radius.

The lattice parameter, or a_0 , of cubic crystals can be determined from Θ and the angle between the incident and reflected beam by means of Cohen's method (14), derived for the back-reflection focusing camera:

$$\sin^2 \Theta = \frac{\lambda^2}{4a_0^2} (h^2 + k^2 + l^2) + D \phi \sin \phi$$

λ = the wave length of the reflected beam

h , k , and l are the indices of the reflecting plane

D = a constant, different for each film

ϕ = the angle between the incident and reflected beam

The $D \phi \sin \phi$ term in the above equation is a correction factor eliminating the dependence upon the a_0 of a calibrating material as well as the errors inherent in the apparatus, such as film shrinkage or expansion, finite slit width, and small displacements of slit and sample from the camera circumference. Since reflections from at least two planes are necessary for the determination of D and only one, from the (3 1 0) plane, was obtained from the alloys, gold powder was added to each sample. The (3 3 1) and (4 2 0) gold lines were used to determine the D values for each film.

All measurements were made directly on the film by means of a Gaertner traveling micrometer, the accuracy of measurement being limited by the precision with which the centers of the lines could be located. In view of the sharpness of the lines obtained in all cases, it is believed that the centers were located to the nearest 0.1 millimeter. An error of 0.1 millimeter in the film measurement results in an error of 0.00008 Angstrom units in the calculated a_0 value for iron. The close agreement of the results obtained from repeated measurements of the lines produced by both the $K\alpha_1$ and $K\alpha_2$ radiations of cobalt indicate that the a_0 values may be considered accurate to within ± 0.00005 Angstrom units.

A record of sample temperatures was kept, and they were found to vary less than 1 degree Cent. during the exposure period. The average temperature during all exposures was 78.8 degrees Fahr.

Table I

The Ferrite Lattice Constant at 26 Degrees Cent. As Affected by Molybdenum Content

Molybdenum Per Cent	a_0 Angstrom Units
0.001*	2.86063
0.164	2.86107
0.230	2.86123
0.342	2.86139
0.478	2.86155
0.714	2.86177
0.899	2.86198

*The value given for pure iron was obtained from the electrolytic iron, which is the basis for these alloys and is to be used in all future work on ternary alloys, melted in a manner identical with that described above.

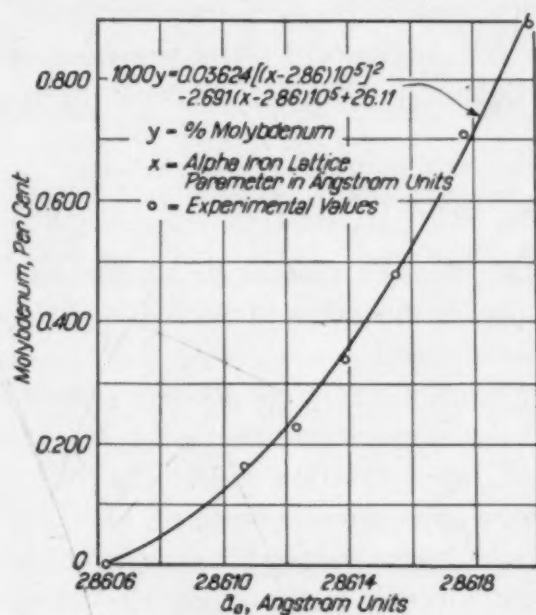


Fig. 1—The Lattice Parameter of Alpha Iron as Affected by Molybdenum.

(26 degrees Cent.), and no temperature corrections were necessary.

The experimentally determined values of the alpha iron lattice constants with the corresponding molybdenum contents are listed in Table I. The relationship is shown graphically in Fig. 1. An empirical equation of the form $y = Ax^2 + Bx + C$ may be fitted to the data and used to predict the molybdenum content. The method of least squares was applied in order to obtain the constants. The derived equation, in the form suitable for computation, is

$$1000y = 0.03624[(x - 2.86)10^5]^2 - 2.691(x - 2.86)10^5 + 26.11$$

where y is the per cent molybdenum and x is the alpha iron lattice constant in Angstrom units. The maximum deviation of the data

from the computed curve is 0.03 per cent molybdenum, and the standard deviation is 0.015 per cent molybdenum.

The alloys used in the present work contained from 0.005 to 0.012 per cent carbon, or approximately the maximum solubility of carbon in ferrite at room temperature. The small variations of the experimental values from the derived curve seem to indicate that the effect of changes in carbon content in this range is less than the experimental error and may be neglected. This is borne out by the work of Burns (11). It is realized, however, that strict use of the curve of Fig. 1 to determine the partition of molybdenum in iron-carbon-molybdenum alloys necessitates the assumption that the solubility of carbon is not increased by the presence of molybdenum. This point will be definitely cleared up during the course of future work.

SUMMARY

1. The problem of the partition of molybdenum between the ferrite and carbide phases in steel is presented, and the desirability of such information is indicated.

2. The earlier work done in connection with the problem and the methods used by the investigators are briefly considered. The adaptability of the X-ray diffraction method to the problem is indicated and the proposed application is outlined.

3. The alpha iron lattice parameter versus molybdenum content relationship to be employed in determining the partition of molybdenum between ferrite and carbide in iron-carbon-molybdenum alloys has been established.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor Lars Thomassen, of the University of Michigan, for his advice and suggestions pertaining to the X-ray data, and to Mr. R. H. Maurer, of the analytical laboratory of Climax Molybdenum Company, for making the chemical analyses of all samples.

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DISCUSSION

Written Discussion: By F. R. Morral, assistant professor of metallurgy, Pennsylvania State College, State College, Pa.

The first X-ray work on the iron-molybdenum system to be published was in 1923 shortly after this new technique was applied to the study of alloys. Bain¹ stated that the lattice parameter of iron did not change when molybdenum dissolved in it. Wever² claimed that the lattice parameter of iron with molybdenum in solid solution followed Vegard's law between 0 and 6 per cent atomic molybdenum. Chartkoff and Sykes³ noted that molybdenum expanded the lattice of iron 1.3 per cent at saturation (22 per cent). It is of interest, therefore, to see published the data of these authors because of its usefulness not only for their purpose but also in other work, such as that of Austin.⁴

The authors mention the double carbide of iron-molybdenum which has

¹E. C. Bain, *Chemical and Metallurgical Engineering*, Vol. 28, 1923, p. 21.

²F. Wever, *Zt. f. Metallkunde*, Vol. 20, 1928, p. 366.

³Chartkoff and Sykes, *Transactions, American Institute of Mining and Metallurgical Engineers*, Vol. 89, 1930, p. 566.

⁴C. R. Austin, "Effect of Elements in Solid Solution on Hardness and Response to Heat Treatment of Iron Binary Alloys", *TRANSACTIONS, American Society for Metals*, Vol. 31, 1943, p. 321.

been found in tool steel⁵ and in magnet steels,⁶ the atomic structure of which has been established by Westgren.⁷ No mention is made of another double carbide which has been found in iron-rich iron-molybdenum-carbon alloys.⁸ This carbide has been designated $(\text{Fe}, \text{Mo})_{23}\text{C}_6$ because of its atomic structure analogy with Cr_{23}C_6 .⁹ Some time ago considerable work was done on the iron-tungsten-carbon¹⁰ alloys to determine the range of this type double carbide in this system. Very little was done on the iron-molybdenum-carbon system beyond establishing its presence. The table below gives the data obtained.

Composition of Alloy by Analysis in Per Cent		Treatment in Vacuum of Electrolytic Residue	Lattice Parameter of $(\text{Fe}, \text{Mo})_{23}\text{C}_6$ in Å
Molybdenum	Carbon		
2.0	1.1	800 Degrees Cent. for 3 hours and quench	10.52 ₇
2.1	1.7	800 Degrees Cent. for 3 hours and quench	10.52 ₇

In the iron-tungsten-carbon series where the percentage of carbon was higher than the tungsten only cementite was found. While with as low as 0.78 per cent tungsten and 0.36 per cent carbon, the $(\text{Fe}, \text{W})_{23}\text{C}_6$ phase was established by X-ray diffraction.

Written Discussion: By John F. Eckel, associate professor of metallurgy, Purdue University, Lafayette, Ind.

It is always gratifying to see scientific work done which will help clear up broad generalizations. Such generalizations are commonly made concerning the partition of alloying elements in steel between the alpha and carbide phases, primarily because of the lack of quantitative information. For this reason, I think we can all agree with Messrs. Bowman, Parke and Herzig when they state that there is a need for the type of information they have undertaken to obtain.

In reading this paper, I was particularly impressed by the care and thought used in attacking a difficult problem which has defied investigators for many years. They have very wisely chosen alloys of high purity, and selected the X-ray method in order to obtain significant quantitative data. Data obtained from such alloys will substantially contribute to our knowledge of the iron-molybdenum-carbon ternary system.

Probably the most difficult phase of an investigation of this nature, which employs alloys of high purity, will be the application of the data obtained to commercial steels. Such an application must be made with due consideration to the presence of larger quantities of impurities. It is only necessary to consider briefly the elements commonly encountered in commercial steels for an insight into the complexity of the task. For instance, silicon, manganese, phosphorus and copper are soluble in the alpha phase, and these elements are common in modern steels. Hence, such questions as the following must be answered before an investigation of this nature can be considered complete. What will

⁵Westgren and Phragmen, "On the Double Carbide of 'High Speed Steel'", *TRANSACTIONS, American Society for Steel Treating*, Vol. 13, 1928, p. 539.

⁶W. A. Wood, *Philosophical Magazine*, Series 7, Vol. 10, 1930, p. 659.

⁷A. Westgren, *Jernkontorets Annaler*, 1933, p. 1.

⁸F. R. Morral, A. Westgren and G. Phragmen, *Nature*, Vol. 132, 1933, p. 60.

⁹A. Westgren, *Jernkontorets Annaler*, 1934, p. 154.

¹⁰Unpublished.

be the effect of these elements individually or collectively upon the lattice parameter of the alpha phase, when molybdenum and carbon are present? Will they materially affect the solubility relationships? If so, what will be the effect upon the partition of molybdenum?

It is hoped that the work which has so admirably been started, will be continued, and that this paper will serve as a stimulant to obtain partition data on other alloying elements.

Written Discussion: By Robert F. Mehl, director, metals research laboratory and head, department of metallurgy, Carnegie Institute of Technology, Pittsburgh.

The authors are undertaking a very worth-while problem, and approaching it is the only way which will provide knowledge quantitative enough to be of real use in rationalizing the effect of alloying elements upon the rate of formation of pearlite and thus upon hardenability. The partition of the alloying element between carbide and ferrite is one of the factors which must be known, if the effect of the alloying element upon the rate of nucleation and the rate of growth of pearlite is to be understood.

Some years ago in a graduate seminar we reviewed the available information on the analysis of carbides in steel. There has been a good deal done, of course, mostly by the use of the residue analysis method and chiefly for the purpose of identifying the chemical nature of the complex carbides in highly alloyed steels. The data thus far obtained are by no means good; they frequently are not good enough to fix upon a formula, and for a determination of the partition of an alloying element between carbide and ferrite they are clearly inadequate. This whole field of the analysis of carbides in steel cries for attention of the competent analytical chemist; so many metallurgical problems, of which this is an important but only one, stand in the need of new and better analytical methods that an analytical laboratory could be kept profitably busy for years. The analytical chemist was once a very important man in the metallurgical field. With many new metallurgical fields uncovered, he should again be called into the metallurgical group. It is very probable that old problems will have to be attacked in new ways, but since science has advanced so much in recent years, it should be possible to develop some wholly new modes of attack.

The use of the lattice parameter is such a method, and since it is observed that a_0 in this system changes appreciably with composition, should yield valuable data. I wonder whether the authors have obtained any partition data since submitting these papers, if so, it would be very entertaining to hear of them.

Such data will fit nicely into reasoning about the factors controlling the rate of formation of pearlite. The problem of the factors controlling the rate of formation of pearlite in simple carbon steels is by no means wholly clarified, even though it is a simpler problem. Since the rate of formation is compounded from the rate of nucleation and the rate of growth, it would be pleasant to be able to calculate these in terms of the known rate of diffusion of carbon in austenite, but there are mathematical-analytical problems of considerable difficulty in this. The rate of nucleation, N , and the rate of growth, G , may be

readily measured and the effect of austenite grain size on these has been clearly established; the manner in which the N and G co-operate to determine the rate of formation has been precisely formulated, so that some progress has been made in a quantitative attack on the problem. But it has not yet been possible to calculate N from the diffusion coefficient of carbon in austenite, and until something is known concerning interface energies it is highly unlikely that much real progress can be made; here is a problem for the modern physicist (we now have both the chemist and the physicist working for the metallurgist!). Nor is it possible to calculate G from the diffusion coefficient of carbon in austenite; at first blush this would seem to be a simpler problem, for it would appear to be necessary to derive the proper concentration gradients in the austenite ahead of the edge of the pearlite colonies into which the lamellae grow edgewise. But the lamellae do not grow edgewise only, but also sidewise, and this sidewise growth must involve repeated nucleation and the calculation of its rate must therefore involve the same problems as these in the calculation of N; moreover, the problem of calculating pure edgewise growth is not so easy, for mathematically it involves a moving boundary, the interface moves, and this has not yet surrendered to analysis. If all this appears pessimistic, it should be remembered that much progress in the whole problem has been made, and that many a difficult problem often surrenders more promptly than we expect.

I have outlined this only to attempt to place the question of partition in proper relation to the whole problem in my own mind. In the case of alloy steels the same problems obtain, to which is added the problem of the diffusion of the alloying element, in which the question of partition is essential. I believe, as the authors do, that this can be attacked only in an experimental way and cannot now be derived theoretically; it might be well to outline the kind of findings to be expected. In a given ternary alloy steel, the partition of alloying element between carbide and ferrite will have an equilibrium value at a given temperature: at equilibrium a given fraction of alloy will be associated with the carbide and the rest with the ferrite; the partition coefficient at equilibrium in the general case will change with temperature. The equilibrium partition coefficient will obtain on holding the sample at a given temperature for effectively infinite time. But during the course of the formation of pearlite from austenite, the partition coefficient may be quite different from the equilibrium coefficient: there is no requirement that it be the same. The degree of departure from the equilibrium coefficient might well vary with temperature. In an experimental attack the equilibrium coefficient should be determined first and then the coefficient as observed during and at the end of the pearlite reaction. Furthermore, while the equilibrium partition coefficient may not vary with changes in composition of the alloy, that coefficient observed just at the end of the pearlite reaction may vary with composition, and this variation would have to be taken into account in explaining the effect of increasing amounts of alloy upon the rate of formation of pearlite.

Such knowledge would be of real usefulness in increasing our understanding the complicated effects of alloying elements on the rate of formation of pearlite. It is fortunate that the problem is in the hands of the present authors.

Authors' Reply

The interest shown by the discussions is very stimulating, and all those participating are thanked sincerely by the authors.

We especially appreciate the interest shown by Dr. Morral in calling to our attention his evidence for the existence of a second cubic double carbide in the iron-molybdenum-carbon system. Although its presence in alloys of the composition range under consideration at present has not been established, the fact that a similar carbide has been found in the low-carbon, low-tungsten region of the iron-carbon-tungsten system serves to indicate the need for establishing the existence or non-existence of this phase in the alloys currently being studied.

The point brought up by Professor Eckel relative to the difficulties of applying data obtained from ternary alloys to the partition of molybdenum in commercial steels is very pertinent, and is recognized by the authors. However, if it can be shown by studies on the ternary alloys that molybdenum itself must diffuse during the transformation of austenite to ferrite and carbide aggregates, it may be unnecessary to investigate the effects of the common impurities insofar as our understanding of the mechanism whereby molybdenum increases hardenability is concerned.

We wish to thank Dr. Mehl for his discussion of the need for further information concerning the distribution of the added elements in alloy steels. Any attempted explanation of the decrease in transformation rates affected by most alloy elements seems to rely on one of two effects, either a decrease in the diffusion rate of carbon or the necessity for the diffusion of the added element itself. Evidence at hand indicates that the entire explanation may not lie in the rate of diffusion of carbon, and it is hoped that the results of the current study will establish a basis upon which the merits of the second explanation can be judged.

Regarding the availability of actual partition data, very little information has been obtained as yet; the little we have is the result of preliminary work with the chemical separation method, carried on by Mr. R. H. Maurer of the analytical laboratory of Climax Molybdenum Company. Although these results are open to the criticism generally given to carbide data obtained in this manner, they are considered to be sufficiently accurate to indicate a tendency, and for that reason they may be profitably presented. The steel employed in the investigation contained the following major constituents:

	Per Cent	
Carbon	0.70	
Manganese	0.89	
Silicon	0.23	
Molybdenum	0.22	
Treatment	Per Cent Molybdenum in Carbide	Per Cent Molybdenum in Ferrite
Quenched, drawn 24 hours at 1300 Degrees Fahr.	1.11	0.10
Completely transformed isothermally at 1280 Degrees Fahr.	1.14	0.095
Completely transformed isothermally at 1200 Degrees Fahr.	0.99	0.14

Attempts were made to obtain similar data on material transformed at lower temperatures; but, owing to the instability of the carbides formed, the results are not considered to be of sufficient accuracy to warrant their use here.

Dr. Mehl's point relative to the possibility of the partition coefficient effective at equilibrium being different from that found at the end of the transformation is well taken. It might reasonably be expected that during transformation, especially at temperatures where the rate is extremely rapid and the opportunity for diffusion of the added element is very slight, the distribution would be determined solely by chance. If this were true, the alloy content of the ferrite and carbide should be approximately equal when compared on a basis of weight per unit volume. The data given above indicate that the carbide is decidedly richer in molybdenum, and consequently suggest the existence of a driving force which exerts its influence during the transformation reaction. While the nature of this driving force cannot be determined, on the evidence at hand it does not seem unlikely that it is a function of the carbide-forming properties of molybdenum acting in conjunction with the rate of diffusion of the element. If such is the case it might well be, as Dr. Mehl suggests, that the partition coefficient would change after the transformation reaction had been completed and that the molybdenum would concentrate in the carbide as the holding time increased.

Since the factors which directly influence the transformation reaction are essential to an understanding of hardenability, it becomes obligatory to investigate these factors during and at the end of the reaction as well as at equilibrium.

THE EFFECT OF MODERATE COLD ROLLING ON THE HARDNESS OF THE SURFACE LAYER OF 0.34 PER CENT CARBON STEEL PLATES

BY HARRY K. HERSCHMAN

Abstract

The influence of moderate cold rolling on the surface indentation hardness of 0.34 per cent carbon steel plate initially surface finished by three different methods was investigated. Variations of the hardness of the surface layers extending to different depths below the surface of the specimens were determined by applying different loads on a Knoop indenter. Indentation hardness tests also were made with the Rockwell superficial hardness machine. The results obtained with the Knoop indenter showed significantly lower hardness numbers for the superficial layer of the steel after the lighter degrees of rolling, the magnitude of change apparently being influenced by the mode of initial finishing. Hardness decreases were not revealed by tests made with the Rockwell superficial machine nor in any case in which the penetration of the Knoop indenter exceeded about 0.0003 inch.

INTRODUCTION

IN co-operation with the Bureau of Engraving and Printing, the National Bureau of Standards is studying the effect of different surface finishes on the engraving and transferring properties of 0.34 per cent carbon steel plates. A previous paper (1)¹ on the initial phase of this study described results of surface indentation hardness tests made with an elongated pyramidal diamond (Knoop) indenter (2) on specimens having different metallographic structures and finished under different grinding conditions. Exploratory experiments with these specimens indicated that burnishing the surface by cold rolling was accompanied by a decrease in hardness of the superficial layer. This appears to be in accord with recent work of Goss and Brenner (3), who presented hardness (Monotron test)

¹The figures appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Twenty-fourth Annual Convention of the Society held in Cleveland, October 12 to 16, 1942. The author, Harry K. Herschman, is metallurgist, National Bureau of Standards, Washington, D. C. Manuscript received May 9, 1942.

data showing a hardness reversal during continued cold rolling of 0.74 per cent carbon (sorbitized) steel. However, similar experiments by these investigators with this steel in the pearlitic condition showed only progressive hardening. A behavior similar to that of sorbitic steel, reported by Goss and Brenner, has been found also in copper, by Atkin (4) and others (5), (6). Thompson (7) who observed no indication of hardness reversals during the progressive cold rolling of either mono- or polycrystalline copper briefly summarized a number of suggestions offered by other concurring investigators to account for the apparent anomalous behavior of copper. However, these suggestions apparently did not take into consideration the differences in the properties of the metal immediately adjacent to the surface compared with the metal more remote from the surface as a possible factor influencing hardness tests involving shallow indentations. That such a layer which possesses distinctive characteristics exists has been borne out by considerable research since Beilby (8) first postulated the formation of an amorphous layer on metals subjected to polishing and other means of cold working. Because of the distinctive characteristics of the metal near the surface that has been cold-worked, it is reasonable to assume that the results of the hardness tests will be influenced by the depth of penetration of the indenting tool.

The structure of the surface layer of 18-8 stainless steel has been shown by Wulff (9) to be affected to different degrees by different surface finishing procedures. This is in accord with the results of Chalmers (10), who found, by optical reflectivity means, significantly different surface hardness values for annealed copper polished with different abrasives. These results suggest that the initial surface finish of a metal may influence the magnitude of the hardness changes in its surface layer caused by light cold rolling.

This paper summarizes the results of indentation hardness tests made with the Knoop indenter (2) penetrating to progressively increasing depths beneath the surface of specimens, initially finished by different methods and then cold rolled to different degrees. These data are supplemented by results of hardness tests made on the same specimens with the Rockwell superficial hardness tester.

MATERIAL

The steel investigated was representative of that used for rotary

press printing plates by the Bureau of Engraving and Printing with respect to both composition and microstructure. The significant constituents, other than iron, determined by chemical analysis were as follows:

Constituent	Per Cent
Carbon	0.34
Manganese	0.48
Phosphorus	0.04
Sulphur	0.04
Silicon	0.20

These plates are hot-rolled and then annealed, and in this condition the metal at, and in, the immediate vicinity of the surfaces usually is nearly free of carbon. In preparing the plates for engraving and transferring, the decarburized layer is completely removed from the side used for transfer purposes by grinding. However, this precaution is not required in finishing the other side of the plates. The typical microstructures of the metal near the surface on the two sides of a transfer plate are shown in Figs. 1a and 1b, respectively.

The parent test bars used in this study were cut from a single plate of steel to the dimensions $4\frac{1}{2}$ by 1 by $\frac{1}{4}$ inch thick. Each of the test bars prior to cold rolling was surface finished by one of three different methods as follows:

- (a) Wet grinding with a soft alundum abrasive wheel, No. 46 grain, vitrified bond; maximum depth of roughing cuts 0.0005 inch, finishing cut 0.0001 inch.
- (b)² Surface grinding with a soft wheel and then buffed on a segmented leather "knee" wheel charged with chromic oxide.
- (c) Wet grinding as (a) above, 2 stages on the tin-lead laps, first with No. 302 abrasive and then with No. 303 $\frac{1}{2}$ abrasive and final polishing on velvet charged with a paste of optical rouge in water.

The surface of the plate studied in most cases corresponded to the side of the plate which was free of the decarburized layer. However, metallographic examination frequently has revealed large areas of free ferrite at the transfer surfaces of plates, attributable to various causes. In order to study the effect of rolling on this type of structure, the decarburized side of a series of specimens was polished by method (c) as described above.

²Representative of the finishing treatment applied by the manufacturer of transfer plate used for the present study.

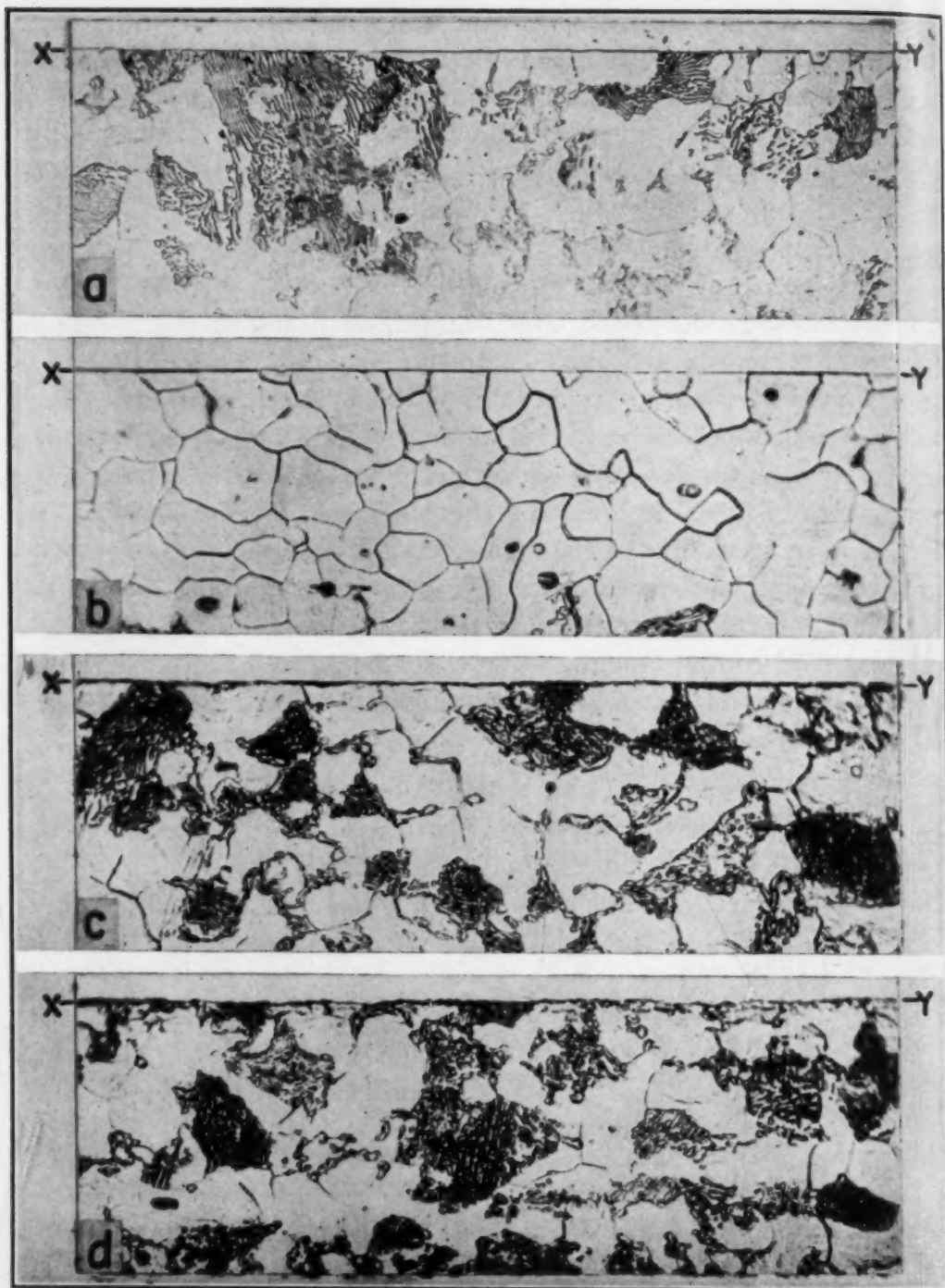


Fig. 1—Characteristic Structure of Specimens of Annealed 0.34 Per Cent Carbon Steel as Initially Surface-finished by Different Methods, Observed in Each Case in a Section Perpendicular to the Surface Under Consideration, the Trace of Which is Indicated by Line *x y*. a. Surface layer adjacent to transferring surface of plate finished by metallographic polishing. b. Decarburized to a depth of 0.01 to 0.02 inch. Surface finished by metallographic polishing. This is characteristic of the surface layer of the underside of transfer intaglio printing plates. c. Surface layer adjacent to transferring surface of plate, finished by buffing. d. Surface layer adjacent to transferring surface of plate, finished by grinding.

The surfaces (indicated by trace *x y*) of the polished specimens (micrographs a and b) were smooth as compared with those of the specimens buffed and ground, respectively (micrographs c and d). Micrographs a, c and d show the microstructural inhomogeneities of the metal adjacent to the test surface (trace *x y*) of the specimens. All specimens were etched in 1 per cent nital. $\times 500$.

METHODS OF TEST

Rolling Treatments—All cold rolling was done on a two-high rolling mill, power-driven, equipped with hardened steel rolls having a diameter of 5 inches. The specimens were reduced approximately 0.0005 inch in thickness for each pass.

A specimen $\frac{3}{4}$ inch long was cut from each test bar, as initially surface finished, and used for hardness tests of the steel in the pre-rolled condition. The remainder of each bar (about $3\frac{3}{4}$ by 1 by $\frac{1}{4}$ inch thick) was cold-rolled to 1 per cent reduction in thickness. A coupon approximately $1\frac{1}{4}$ inches in length was then cut from each bar and reserved for hardness tests. This procedure of rolling and sampling was repeated for nominal reductions of 2 and 4 per cent.

Indentation Hardness Tests—Hardness tests were made with both the Knoop indenter, used with the apparatus described in a previous publication (2) and the Rockwell superficial hardness tester. The usefulness of the elongated pyramidal diamond (Knoop) indenter for determining hardness gradients in the surface layer of steel was discussed in the above-mentioned publication (2). Since preliminary tests suggested that the hardness gradient might be confined to a thin layer immediately below the surface, correspondingly shallow indentations were required to reveal significant changes in hardness in this layer. The smallest load which could be used on the indenter with accuracy, for the apparatus employed, was 50 grams.

Indentation tests with 50, 100, 200, 500, 1000 and 2000-gram loads on the indenter were made on the finished surface of each specimen. The time of contact of the indenter with the specimen in making a test was 20 seconds. All indentations were made so that the long axis was nearly parallel to the direction of rolling and to the scratch marks on the specimens formed during the initial surface finishing.

RESULTS AND DISCUSSION

The results of the Knoop indentation tests determined with different loads on the indenter for each of the specimens before and after rolling are listed in Table I. These data graphically presented in Figs. 2 to 5 show the average hardness changes with each load, which occurred during the progressive stage of rolling. In this

Table I

Average Indentation Hardness (Knoop and Rockwell Superficial) Numbers of 0.34 Per Cent Carbon Steel Specimens (1) As Initially Surface Finished and (2) After Moderate Cold Rolling to Different Degrees

Initial Surface Finish	Reduction by Cold Rolling Per Cent	Indentation Hardness Number Knoop Indenter ^(a) Test Load, Grams						Rockwell Superficial 15T ^(b)
		50	100	200	500	1000	2000	
Metallographic polish (no decarburized layer at surface)	0	164	154	148	144	142	139	83
	1	151	145	142	147	145	140	85
	2	170	175	166	164	157	156	86
	4	168	174	168	166	163	159	87
Metallographic polish (decarburized surface layer)	0	181	163	159	160	153	143	85
	1	162	156	153	151	157	147	85
	2	154	153	152	153	153	147	85
	4	158	170	175	176	177	168	86
Buffed	0	203	183	176	153	152	149	83
	1	180	180	166	162	158	153	85
	2	182	180	176	170	165	160	85
	4	200	200	181	176	173	166	86
Ground	0	230	227	214	188	168	160	83
	1	226	221	209	184	175	163	85
	2	220	212	200	184	177	167	86
	4	228	220	205	191	183	171	87

Note (a) Each value is the average of 25 to 60 determinations.

(b) Each value is the average of 10 to 15 determinations.

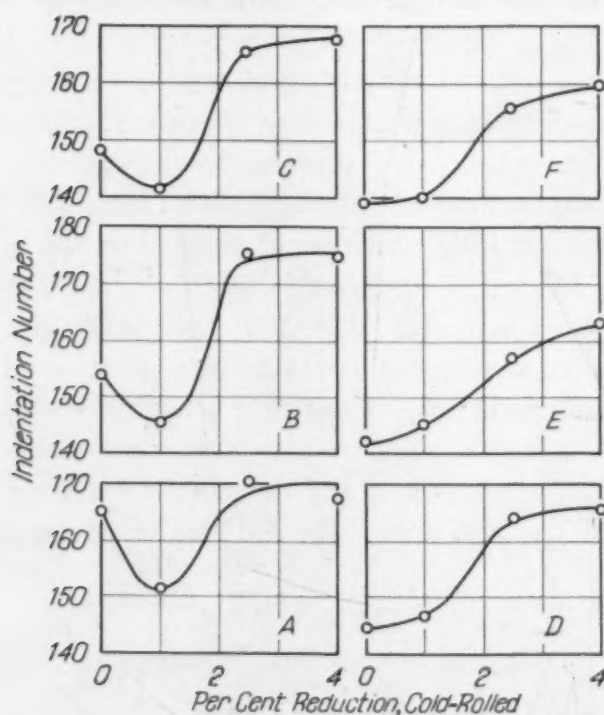


Fig. 2—Influence of Cold Rolling on the Surface Indentation Hardness Values (Knoop Indenter) of Annealed 0.34 Per Cent Carbon Steel, Initially Finished by Metallographic Polishing.

Curve	Load on the Indenter, Grams	Curve	Load on the Indenter, Grams
A	50	D	500
B	100	E	1000
C	200	F	2000

manner, the effect of rolling on the hardness of layers differing in thickness can be shown. The curves (A, B and C, Figs. 2 to 5) show in most cases that the hardness number determined with the 50, 100 and 200-gram loads on the specimens after cold rolling to 1 and 2 per cent reductions were significantly less than they were prior to rolling. However, these same curves in general show a

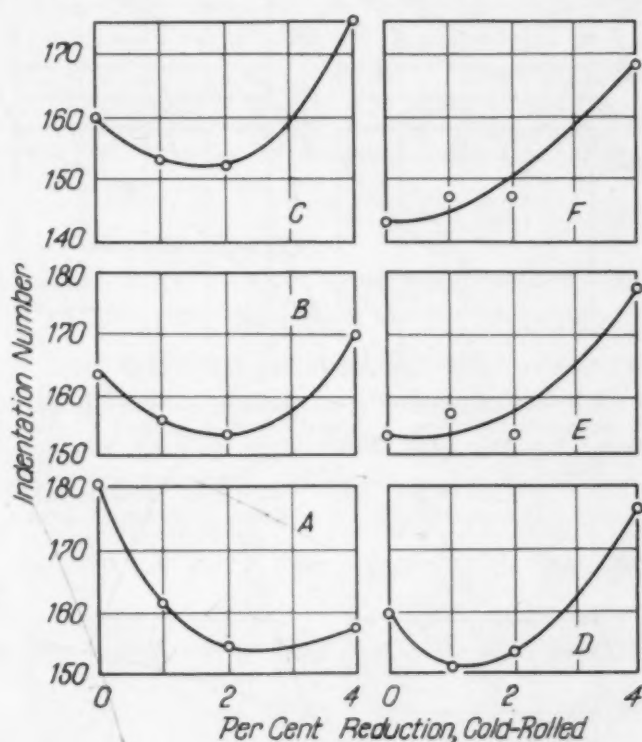


Fig. 3—Influence of Cold Rolling on the Surface Indentation Hardness Values (Knoop Indenter) of Annealed 0.34 Per Cent Carbon Steel, Initially Finished by Metallographic Polishing. The Test Specimens in This Case Had a Decarburized Surface Layer 0.01 to 0.02 Inch in Depth.

Curve	Grams Load on the Indenter
A	50
B	100
C	200
D	500
E	1000
F	2000

progressive increase in hardness for reductions greater than 2 per cent. This indicates that there was a decrease in hardness during the initial stages of cold rolling followed by an increase on further rolling for layers penetrated by the indenter with loads of 50, 100 and 200 grams.

The Knoop hardness numbers obtained with the relatively heavy

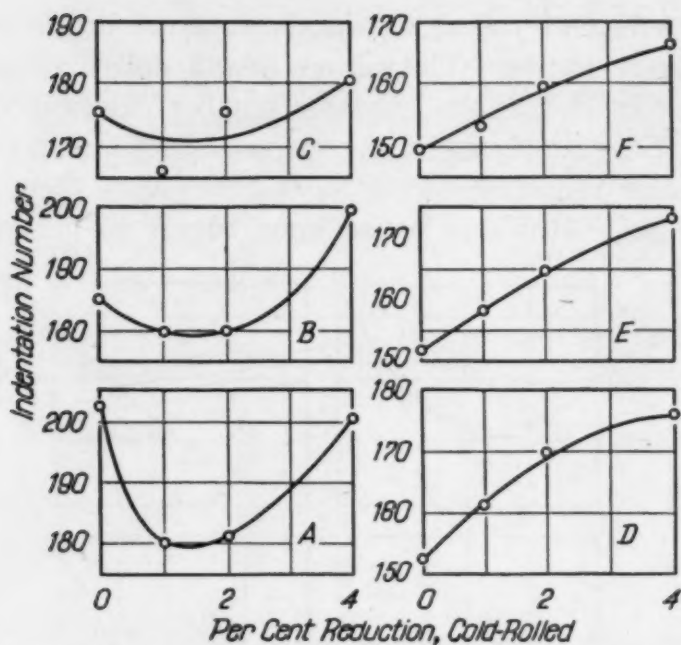


Fig. 4—Influence of Cold Rolling on the Surface Indentation Hardness Values (Knoop Indenter) of Annealed 0.34 Per Cent Carbon Steel, Initially Finished by Buffing.

Curve	Load on the Indenter, Grams	Curve	Load on the Indenter, Grams
A	50	D	500
B	100	E	1000
C	200	F	2000

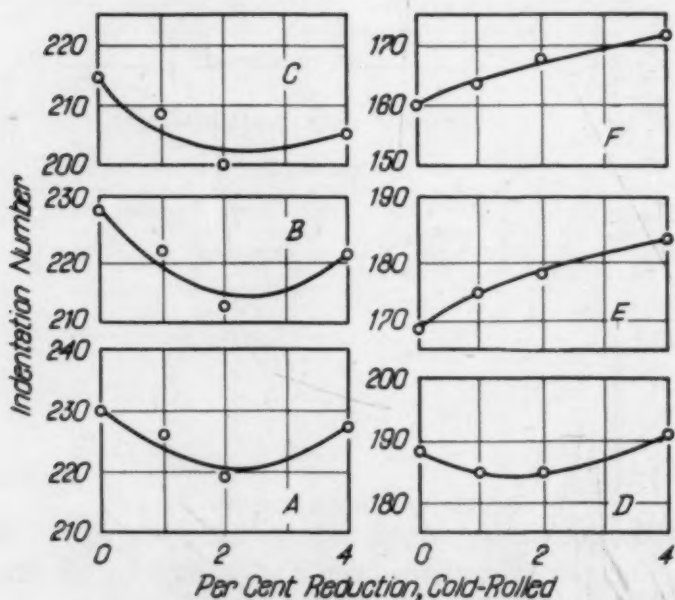


Fig. 5—Influence of Cold Rolling on the Surface Indentation Hardness Values (Knoop Indenter) of Annealed 0.34 Per Cent Carbon Steel, Initially Finished by Grinding.

Curve	Load on the Indenter, Grams	Curve	Load on the Indenter, Grams
A	50	D	500
B	100	E	1000
C	200	F	2000

Table II

Relationship of Indenting Load to Depth of Penetration Below the Surface of Annealed 0.34 Per Cent Carbon Steel Plate in the Moderately Rolled and Pre-Rolled Conditions

Load, Grams	Approximate Average Depth of Penetration of the Indenter, Upper and Lower Limits ^a in Units of 10^{-6} Inch
50	7 to 9
100	10 to 13
200	15 to 18
500	25 to 29
1000	36 to 41
2000	53 to 58

^aThese values are the limiting computed depths of indentations obtained on specimens initially surface finished by three different methods (grinding, buffing and metallographic polishing) and on companion specimens reduced in thickness 1, 2 and 4 per cent by cold rolling.

loads (2000, 1000, and, in some cases, 500 grams, curves D, E and F, Figs. 2 to 5) show no indication of hardness decreases at any of the stages of cold rolling. These results are in accord with those obtained on the same specimens with the Rockwell superficial tester (15-kilogram load, $\frac{1}{16}$ -inch steel ball; Fig. 6). These data indicate that the indentation numbers obtained under these conditions of test were not appreciably influenced by the hardness of the outermost portion of the surface layer (penetrated with the 50, 100 and 200-gram loads).

The depth of the indentations which indicated "softening" of

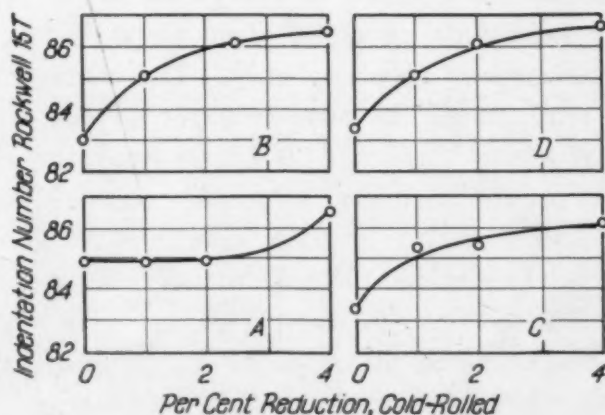


Fig. 6—The Influence of Cold Rolling on the Surface Indentation Hardness Values of the Test Specimens Described in the Legends of Figs. 2 to 5, as Determined with the Rockwell Superficial Hardness Tester, $\frac{1}{16}$ -Inch Ball Indenter, 15-Kilogram Load.

Curve	Initial Surface Finish
A	Polished (surface layer decarburized)
B	Polished
C	Buffed
D	Ground

the surface metal during cold rolling can be calculated, since the depth of the Knoop indentation is linearly related to the length of its long axis (ratio 1:30). The average values for the limiting depth of penetration for the specimens tested, before and after rolling, are listed with the corresponding test load in Table II. A correlation of these values with the Knoop hardness data (Table I) for each load condition suggests that the depth of the metal which significantly decreased in hardness (penetrated with 50, 100, 200 and, in some cases, 500 grams) during cold rolling was less than 0.0003 inch.

Although the trends of the results (Knoop tests) were the same for the surfaces investigated, it is noteworthy that the hardness decreases appear more pronounced for the polished specimens than for those which were buffed and ground. An apparent cause for this difference is suggested by the difference of the microstructures of the surface layer of the specimens (Fig. 1) which show evidence of cold work (darkened edge) for the buffed and ground specimens but not for the polished ones. The work of Wulff (9) suggests that the layer of disturbed metal due to metallographic polishing is very thin (less than 0.00003 inch). However, Thomassen and McCutcheon (11) have shown that the disturbance produced in metal during the preparation of specimens preliminary to polishing (see surfacing treatment No. 3) is not completely removed by a single polishing treatment such as used in the present study. This condition although not detectable in the micrographs (Figs. 1a and b) is probably sufficient to obscure variations expected from very thin layers of disturbed metal developed by polishing only. Therefore, the distinctive microstructural features of the surface layer of the specimens finished by different means, disclosed in Fig. 1, may not be conclusive as an explanation for the hardness differences noted. Another factor which may have had a bearing on these results is the geometric characteristics of the surface which differed for the specimens finished by the different methods. (See profiles, Fig. 1). The significance of this factor with respect to its influence on the depth of penetration of the Knoop indenter has been discussed in a previous publication (1).

The present investigation has not advanced sufficiently to warrant an explanation of the underlying cause of the reversals observed. However, the work of Wood (12) and McAdam and Mebs (13) may be significant in this connection. Wood demonstrated that continuous rolling of metals, particularly of copper, causes an increase in diameter of their X-ray diffraction rings to a maximum following

which there is a diminution to a minimum, the two processes alternating on further cold working. He concluded that the progressive expansion of the lattice accompanying cold work was indicative of cumulative internal stress and that the contraction was associated with the relief of such stress. McAdam and Mebs have shown, in certain cases, evidence of the relief of internal stress in severely cold-worked steel after the application of tensile stresses producing slight plastic extensions (0.001 to 0.003 per cent permanent set). The results cited suggest the possibility of stress relief induced by the cold rolling treatments as a significant factor in causing the hardness reversals observed. This presupposes that the surface layer was internally stressed during the polishing, buffing or grinding treatment. It appears reasonable to assume that such was the case, since it is well known that the surface layer of a metal during mechanical finishing is severely stressed to accomplish the plastic flowing and removing of surface metal characteristic of these treatments.

The possible annealing effect on the surface layer by the heat generated during rolling should be considered in any theory advanced to explain the fundamental cause of the results obtained. However, this does not propose that such factor is independent of the suggested stress relief effects which may be a manifestation of annealing reactions. A wholly satisfactory explanation of the phenomenon observed will require further study.

SUMMARY

1. A study was made to determine the influence of cold rolling on the hardness properties of the surface layer of annealed 0.34 per cent carbon steel plate, initially surface finished by three different methods, grinding, buffing and metallographic polishing. The test surface of the specimens used for most of the work was essentially free of surface decarburization. However, the metal adjacent to the corresponding surface of one series of specimens tested was decarburized to a depth of 0.01 to 0.02 inch.

2. Hardness tests were made on the specimens before and after rolling with an elongated pyramidal diamond (Knoop) indenter under loads of 50, 100, 200, 500, 1000 and 2000 grams, respectively. Hardness tests also were made on the same specimens with the Rockwell superficial hardness tester, by using a 15-kilogram load on a $\frac{1}{16}$ -inch steel ball indenter.

3. The experimental data show that the Knoop hardness number of the surface layer of the steel, distinguished from the underlying metal, was lower after cold rolling reductions of 1 and 2 per cent than it was prior to rolling.

4. Within the limitations of the tests, the results suggested that the most significant hardness decreases which accompanied the lighter degrees of rolling (1 and 2 per cent reductions) occurred in a layer less than 0.0003 inch in thickness.

5. The results obtained with the Rockwell superficial tester in no case revealed a lower indentation hardness for the specimens after cold rolling than was obtained prior to rolling. In this respect the results obtained with the Knoop indenter under loads of 1000 grams (1 kilogram) and 2000 grams (2 kilograms), respectively, were comparable.

6. The test data suggest that the indentation hardness of the surface layer of the steel in the pre-rolled and rolled conditions was influenced by the nature of the initial surface finishing treatment.

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DISCUSSION

V. N. KRIVOBOK:³ The question of measuring the hardness of superficial layers is quite difficult. As a matter of fact, even measuring the hardness of very thin material proves at times quite a problem.

It will be appreciated if there is someone in the audience who could throw light on the manner in which such measurements can be done, avoiding the pitfalls and difficulties, and arriving at the correct answer.

My remarks about the difficulties associated with measuring the hardness of the superficial layer were based on some past experience. As I remember it on several occasions it was found very desirable to measure the hardness, if possible, of the surface of an aluminum alloy because by so doing it was hoped to ascertain whether or not specific surface heat treatments were affecting only the very surface or penetrated into the metal to some appreciable degree. Microscopic examination proved to be of no help and it occurred to me that careful hardness determinations may answer our question. Our results were not convincing. I must confess that I overlooked somehow or other the possibility of the Knoop method and I am really grateful to Mr. Herschman for bringing this method to my attention.

ERNEST E. THUM:⁴ Of course, there is also a micro-indenter of European extraction which is attached to the microscope's objective; it was exhibited at the National Metal Congress, either last year or the year before. By that means micro-impressions are made under exceedingly light loads, and then measured by filar micrometer on the same microscope.

Without attempting to argue the relative merits of measuring hardness by the scratch method and the indentation method, it is worth remembering that Mr. Bierbaum long ago developed an accurate sclerometer which so far has been used distinctly as a research instrument. In any investigation of surface hardness or of micro-hardness I believe that Mr. Bierbaum's instrument should be considered.

The great difficulty of determining hardness by very small indentations has already been brought out, namely, you cannot check yourself very closely in any material having minor heterogeneities in structure, because of the fact that the test covers such a small amount of material and there is no chance to average the conditions—such as are averaged, we will say, in a Brinell hardness test—except by making a multiplicity of random tests.

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⁴Editor, METAL PROGRESS, Cleveland.

One interesting way of avoiding that was brought out a year or so ago by the Swedish investigator Bo Ljunggren. Published in the Carnegie Research Memoirs by the British Iron and Steel Institute in 1940 it probably has been overlooked by most of us on this side, so it was abstracted in *Metal Progress*, October 1942, page 698. Ljunggren studies the variations in hardness by ruling a grating on a smoothed surface of the metal.

The advantages apparently are many. In the first place, the scribe does not need to be ground to the exceedingly high degree of geometric accuracy that Mr. Bierbaum's instrument requires, and in the second place, the averaging of results is automatic; what the first scratch does not show the neighboring scratches do.

The method evidently is so sensitive that it reveals difference in the hardness of adjoining grains of very pure iron merely due to the fact that the intersecting plane cuts different crystallographic orientations in the neighboring grains. Even such minor differences in soft iron are readily determined by the differences in appearance of the sclero-grating so formed.

It has also been used by the Swedish investigator to study the variation of hardness of nitrided cases with depth below the surface and it shows up very clearly the soft surface which has been frequently suspected of occurring on the very outside of nitrided case, which as a whole might measure only a few thousandths of an inch.

Hardness is shown, by such a sclero-grating, to vary at the grain boundaries in metal which microscopically appears to be a single-phase material, but in which probably some sub-microscopic precipitation of excess constituent has already begun at the grain boundaries. Hardened regions surrounding blow-holes and inclusions were also noted.

So this method, which of course is also only a research method, has a number of interesting features, the first of which is the jewel does not need to be accurately ground, and the second that it is free from the "sampling" effect which is inherent in any test method which picks out a pin point here, there, or the other place.

W. J. CONLEY:⁵ We have done considerable work with the Bierbaum microcharacter. Living close to Mr. Bierbaum, I have had personal contact with him over a number of years. I find that for cold-worked material it is not successful. It is more sensitive to differences in chemical composition, as he mentioned, in the case of precipitation between boundaries. Being a machine-like cut, it does not seem to be sensitive to cold-worked surface hardness and then there is some difficulty in determining the exact width of cut which might show the difference. A rolled up burr-like material is displaced by means of this micro-diamond tool. The equivalent amount of material due to the depth of penetration must be compacted or flowed and rolled up over, and when this is examined at high magnification, as is normally done, it is difficult to determine the width of the cut which would show the difference between soft and cold-worked substances. A focus must be made on the surface of the specimen, thus reading a width which is not exactly what might be called the width of the cut.

⁵Acting chairman, department of engineering, University of Rochester, Rochester, N. Y.

As far as research work is concerned, we find it can be used by a number of people if they take the ordinary care anyone used to a microscope will use, and it can be used in a great variety of materials. We have used the same diamond over a period of eight years and in that time twenty-five different operators have used it. At the present time it seems to have a very fine sharp point.

We have had success with it for determinations such as Mr. Thum spoke about; in finding amounts of phases that are almost submicroscopic in extent, and in recognizing phases that under the microscope could not be brought out by different types of etching. Thus an alloy which is known to be 100 per cent of a given phase can be micro cut, and from average readings across the grains a good idea of the hardness of that particular phase can be had. A cut on something containing the several phases previously determined can be made and used for recognition. We have found it very useful in investigating alloys.

Author's Reply

Replying to Dr. Krivobok, it is recognized that there are many pitfalls to be avoided in securing an accurate determination of the hardness of thin sheet by indentation methods. One of the most common difficulties encountered is caused by the so-called "anvil effect", i.e., the cold working influences of the indentation penetrate the entire thickness of the specimen and are transmitted to the anvil supporting it. Thus it is obvious that the hardness of the anvil may significantly influence the depth of penetration of the indenter and thereby affect the accuracy of the determination. With proper selection of loads on the Knoop indenter hardness tests have been made on very thin sheet without any indications of "anvil effect" due to the very shallow depth of penetration of the indenter. It may be observed in the present paper that the depth of penetration of the indenter in the soft steel investigated was in no case in excess of 0.0003 inch for the 200-gram load and 0.00008 inch for the 50-gram load.

The sensitivity of the Knoop indenter is revealed by results of some recent tests made by the author which indicated significant changes in hardness of the surface layer of specimens (1-inch square section) of annealed carbon steels cold-worked by polishing with rouge only despite the failure of X-ray diffraction to indicate any cold working effects accompanying the polishing treatment.

Because of the relatively small area covered by the Knoop indentation, structural inhomogeneities in a specimen readily influence the results obtained. Thus, in ascertaining the Knoop hardness number of a steel of the structure in the present paper, it is obvious that a large number of tests were necessary in order to obtain a fair average value as representing the surface hardness number of a specimen. So too in making tests on thin sheet the number of check tests required would be governed by the homogeneity of the material.

The author's experience with the Bierbaum tester on cold-worked metals is quite similar to that stated by Professor Conley.

With respect to the micro-indenter referred to by Mr. Thum, it is assumed that he has reference to one of square base form. The symmetrically shaped

indenting tools such as this one or the conical and ball shaped types, yield final indentations (after load release) whose dimensions, due to elastic recovery, differ from those prevailing immediately prior to release of the load on the indenter. Results obtained with the Knoop (elongated pyramidal shaped) indenter indicate that it is possible to make accurate measurements of unrecovered indentations since the change in dimension of their long axis following load release is negligible.

The scratch hardness method, described by Bo Ljunggren, appears promising for the purposes outlined by Mr. Thum. However, there is no reason to suspect that its value for determining the effect of cold work on the hardness of metals would be any greater than that suggested previously for the Bierbaum tester.

